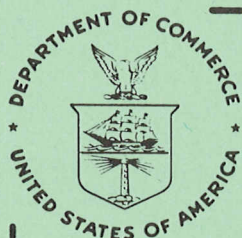


# NOAA Technical Memorandum NMFS-SEFC-30



## NOAA/NMFS FINAL REPORT TO DOE

# Biological/Chemical Survey of Texoma and Capline Sector Salt Dome Brine Disposal Sites Off Louisiana, 1978-1979

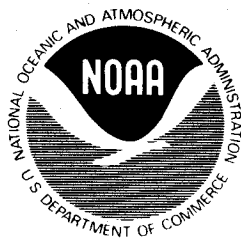
A report to the Department of Energy on work conducted under provisions of Interagency Agreement EL-78-I-O-7146 during 1978-1979.

## Volume VI HYDROCARBONS

NOVEMBER 1980



U.S. DEPARTMENT OF COMMERCE  
National Oceanic and Atmospheric Administration  
National Marine Fisheries Service  
Southeast Fisheries Center  
Galveston Laboratory  
Galveston, Texas 77550



# **NOAA Technical Memorandum NMFS-SEFC- 30**

## **Biological/Chemical Survey of Texoma and Capline Sector Salt Dome Brine Disposal Sites Off Louisiana, 1978-1979**

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### **VOL.VI - DETERMINE HYDROCARBON COMPOSI- TION AND CONCENTRATION IN MAJOR COMPONENTS OF THE ECOSYSTEM**

**BY**

**P.D. Boehm, Ph. D. and D.L. Fiest  
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**A report to the Department of Energy on work conducted under provisions  
of Interagency Agreement EL-78-I-O-7146 during 1978-1979.**

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## Volume VI - HYDROCARBONS

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## LIST OF VOLUMES

This Final Report is printed in nine separate volumes:

### Volume I - BENTHOS

Work Unit 2.1 Describe Living and Dead Benthic (Macro- and Meio-) Communities

Coastal Ecosystems Management, Inc.

R. H. Parker, Ph.D.

A. L. Crowe

L. S. Bohme

### Volume II - ZOOPLANKTON

Work Unit 2.2 Determine Seasonal Abundance, Distribution and Community Composition of Zooplankton

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Volume VI - HYDROCARBONS

Work Unit 3.2 Determine Hydrocarbon Composition and  
Concentration in Major Components of the  
Marine Ecosystem

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Volume VII- TRACE METALS

Work Unit 3.3 Determine Trace Metal Composition and  
Concentration in Major Components of the  
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Southwest Research Institute

J. B. Tillery

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Work Unit 3.4 Determine Seasonal Variations in Inorganic  
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Texas A & M University

J. M. Brooks, Ph.D.

Volume IX - SHRIMP DATA ANALYSIS

Work Unit 5.1 Analysis of Variance of Gulf Coast Shrimp Data

LGL Ecological Research Associates, Inc.

F. J. Margraf, Ph.D.

## INTRODUCTION

In compliance with the Energy Policy and Conservation Act of 1975, Title 1, Part B (Public Law 94-163), the Department of Energy (DOE) implemented the Strategic Petroleum Reserve (SPR). The SPR program was implemented in August of 1977 with the goal of storing a minimum of one billion barrels of crude oil by December 22, 1982. After evaluating several physical storage possibilities, DOE determined that storage in commercially developed salt dome cavities through solution-mining processes was the most economically and environmentally advantageous option.

Six areas along the northwestern Gulf of Mexico were to be investigated as potential storage cavern sites. These areas are shown in Figure 1. This project, "Biological/Chemical Survey of Texoma and Capline Sector Salt Dome Brine Disposal Sites Off Louisiana", deals with proposed disposal sites associated with two of the cavern sites, West Hackberry and Weeks Island. The Biological/ Chemical Survey was initiated in April 1978 and was completed in December 1979. Its major products are Final Reports available through the National Technical Information Service (NTIS), Springfield, Virginia; data files available through the Environmental Data and Information Service (EDIS), Washington, D.C., and any research papers that may be written by participating principal investigators and published in scientific or technical journals. Preliminary results were also made available through DOE/NOAA/NMFS project reviews and workshops attended by project participants and various governmental, private and public user groups.

The objectives of the Biological/Chemical Survey were: (1) to describe the biological, physical and chemical components of the marine ecosystem for each disposal site; and (2) to assess, by analysis of Gulf Coast shrimp data, the importance of the Louisiana shrimping grounds in the vicinity of the proposed salt dome brine disposal sites. These objectives were achieved using historical and new data to describe and quantify the biological, chemical, and physical characteristics and the temporal variations of these characteristics in the environments of each proposed disposal site.

The two proposed disposal sites have been extensively examined, using available meteorological, oceanographic, bathymetric and ecological data, in the following two reports:

Environmental Data Service, DOC/NOAA. 1977.

Analysis of Brine Disposal in the Gulf of Mexico, #2 West Hackberry. Report to Federal Energy Administration Strategic Petroleum Reserve Program Salt Dome Storage. Center for Experiment Design and Data Analysis, NOAA, EDS, Marine Assessment Division, Washington, D.C.

Environmental Data Service, DOC/NOAA. 1977.

Analysis of Brine Disposal in the Gulf of Mexico, #3 Capline Sector. Report to Federal Energy Administration Strategic Petroleum Reserve Program Salt Dome Storage. Center for Experiment Design and Data Analysis, NOAA, EDS, Marine Assessment Division, Washington, D.C.

The above reports and other pertinent documents are available from the Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia, 22151.

Proposed locations of the West Hackberry (Texoma Sector) and Weeks Island (Capline Sector) brine disposal sites are shown in Figures 2 and 3, respectively. These sites are subject to change within the same geographic area pending results of baseline surveys presently underway.

The proposed West Hackberry disposal site is located approximately 9.7 km (6 miles) south off the coast from Mud Lake at Latitude  $29^{\circ}40' N$  and Longitude  $93^{\circ}28' W$  at a bottom depth of about 9 m (30 feet). Operational requirements and engineering limitations of the proposed brine diffuser at this site are as follows: length - 933.3 m (3070 feet); orientation -normal to coast; number of ports - 52; length between ports - 18 m (59 feet); port diameter - 7.6 cm (3 inches); orientation of port riser -  $90^{\circ}$  to bottom; and port exit velocity - 7.6 m/sec (25 ft/sec).

The proposed Weeks Island (Capline Sector) disposal site is located approximately 41.8 km (26 miles) off Marsh Island at Latitude  $29^{\circ}04' N$  and Longitude  $91^{\circ}45' W$  at a bottom depth of about 9 m (30 feet). Operational requirements and engineering limitations of the proposed brine diffuser at this site are as follows: length - 608 m (2000 feet); orientation -normal to coast; number of ports - 34; orientation to port riser -  $90^{\circ}$  to bottom, and port exit velocity - 7.6 m/sec (25 ft/sec).

The Biological/Chemical Surveys in the proposed salt dome brine disposal sites described seasonal abundance, distribution and community

composition of major benthic, planktonic, bacterial and demersal finfish and macro-crustacean ecosystem components; the sediments; the hydrocarbons and trace metals composition and concentration in the marine ecosystem; and the seasonal variations in inorganic nutrients composition and concentration of the water column. The sampling scheme used for sample collections around the two sites is shown in Figure 4. A separate data analysis assessed the importance of shrimp-ing grounds in the vicinity of the proposed brine disposal sites in terms of historical data on species composition, marketing size categories and location of commercial shrimp catches within statistical reporting zones off the Louisiana coast.

Information concerning data from this project is available through the Program Data Manager: Mr. Jack Foreman, Environmental Data and Information Service, Page Building No. 2, 3300 Whitehaven Street, N.W., Washington, D.C.

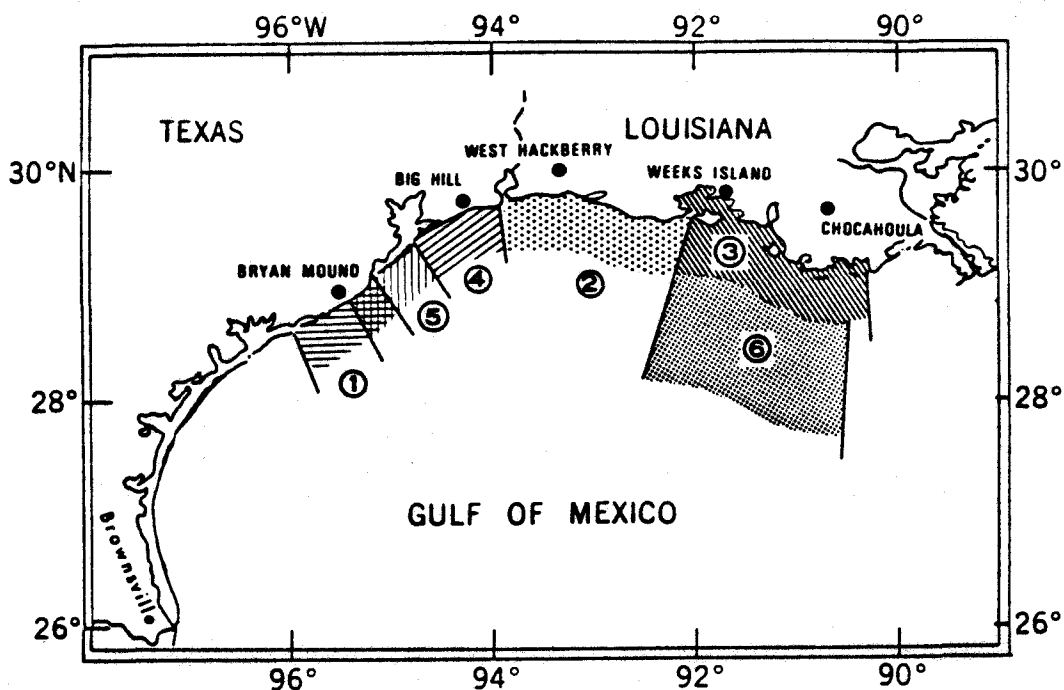


Figure 1. Regions of Study for Brine Disposal Assessment-DOE/NOAA Interagency Agreement (adapted from Environmental Data Service, DOC/NOAA. Analysis of Brine Disposal in the Gulf of Mexico, #2 West Hackberry. 1977.).

- 1 Texas Coastal Ocean, Colorado River to San Luis Pass (Bryan Mound)
- 2 Louisiana Coastal Ocean, Sabine Lake to S.W. Pass of Vermilion Bay (West Hackberry)
- 3 Louisiana Coastal Ocean, S.W. Pass, Vermilion Bay to Timbalier Island (Capline Sector)
- 4 Texas Coastal Ocean, Port Bolivar to Sabine Pass
- 5 Texas Coastal Ocean, Freeport Harbor to Galveston South Jetty
- 6 Louisiana Coastal Ocean, Offshore from Vermilion Bay to Terrebone Bay

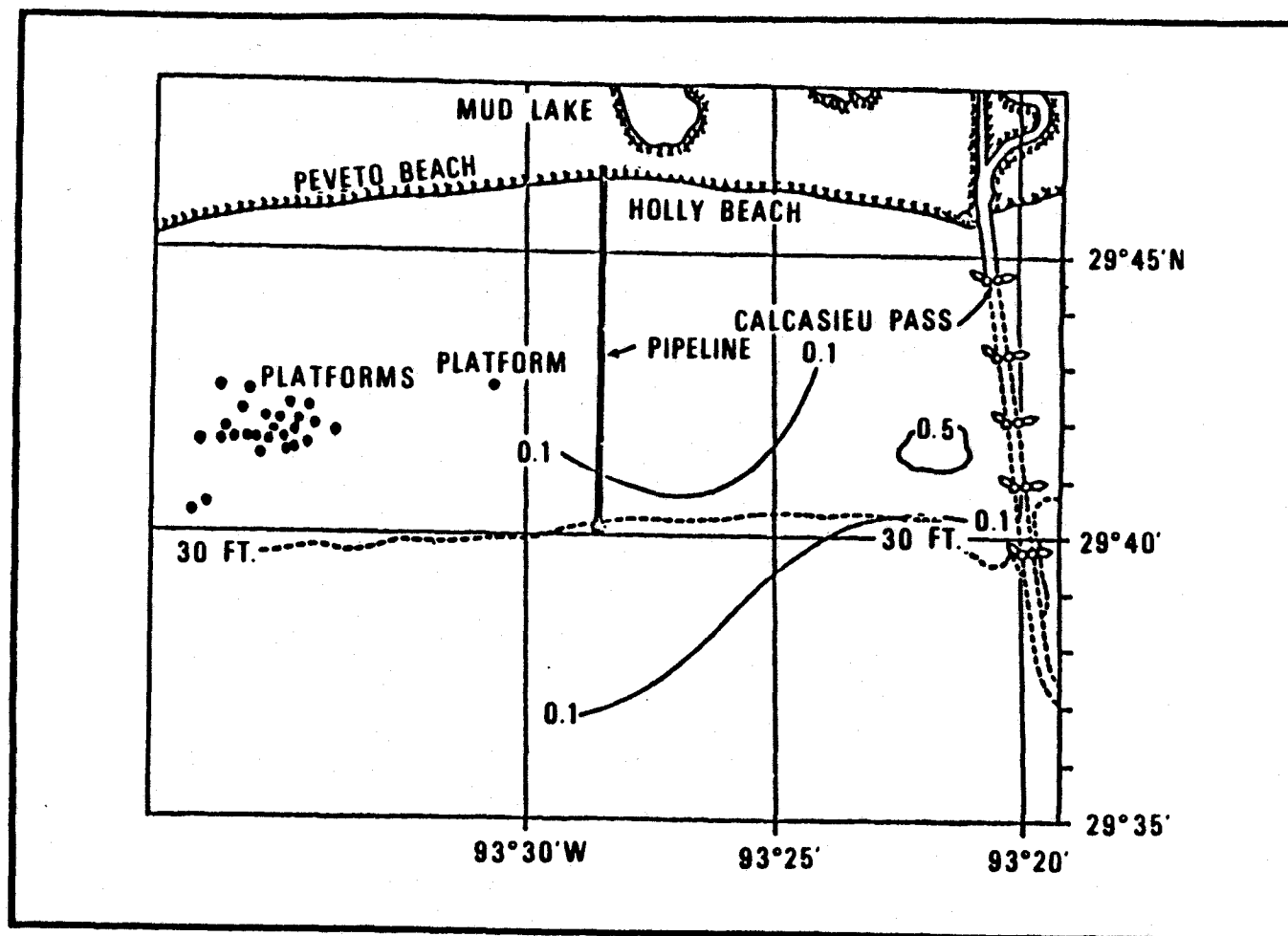


Figure 2. Proposed Texoma brine disposal site.

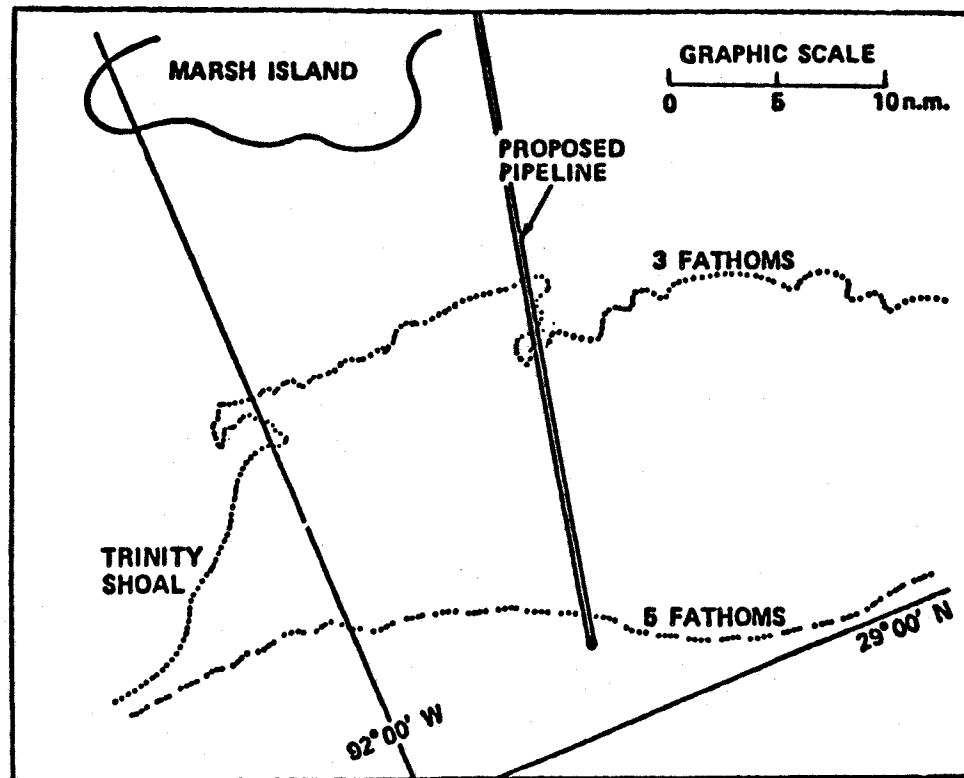


Figure 3. Proposed Capline brine disposal site.



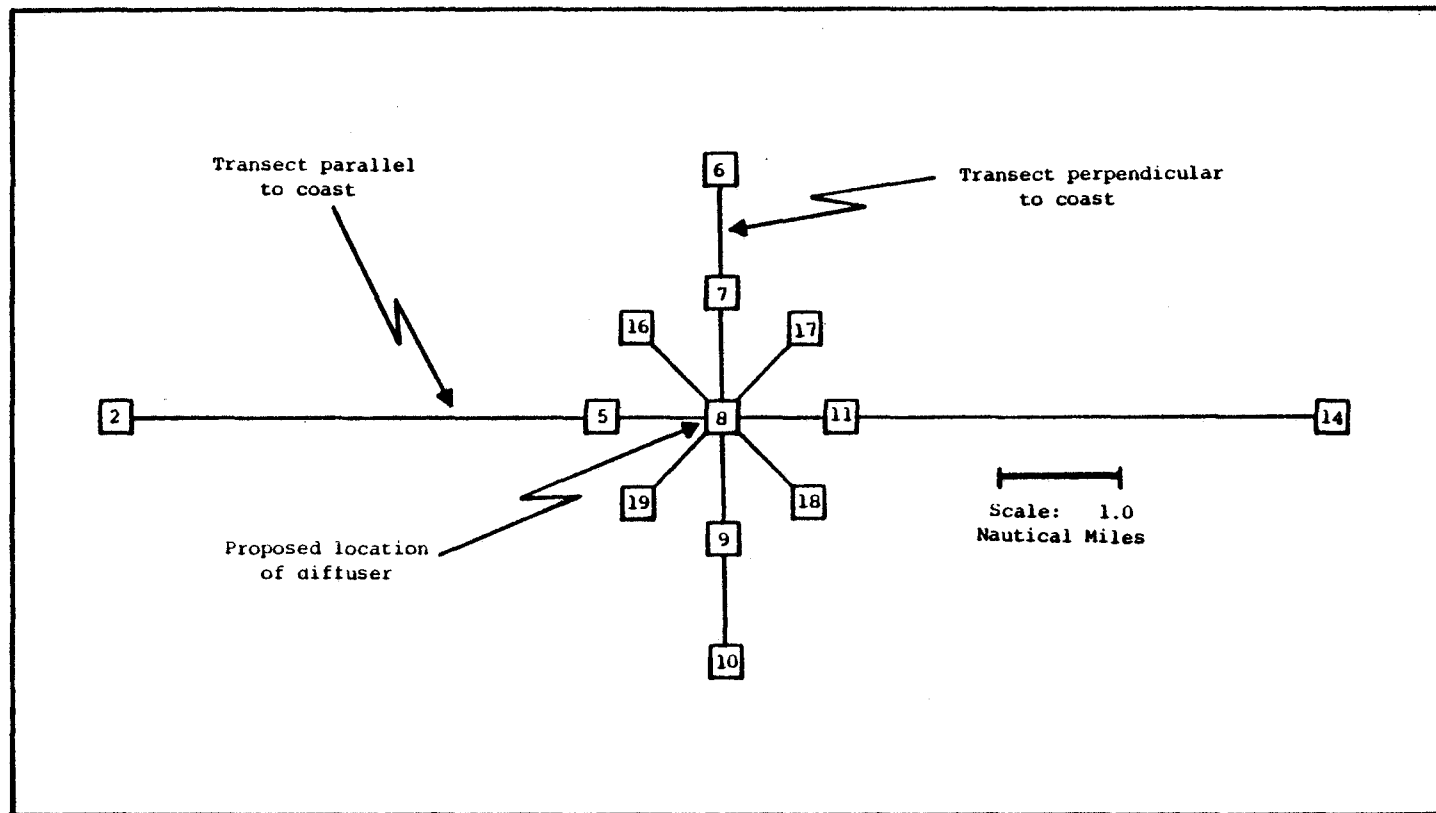


Figure 4. Sampling scheme for proposed salt dome brine disposal sites.

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## II. PRINCIPAL INVESTIGATORS' SECTION

**WORK UNIT 3.2 - DETERMINE HYDROCARBON COMPOSITION AND  
CONCENTRATION IN MAJOR COMPONENTS OF THE  
MARINE ECOSYSTEM**

**P. D. Boehm, Ph.D.  
D. L. Fiest**

**Energy Resources Company, Inc.**

# ABSTRACT

A biological/chemical baseline survey of two proposed salt dome brine disposal sites off Louisiana, West Hackberry and Weeks Island, was conducted from June 1978 to May 1979. Samples of surface sediment, unfiltered seawater, white and brown shrimp and epibenthic organisms were collected during four samplings at five stations located within a 5-mile radius at each site. The hydrocarbon composition of the samples was characterized by glass capillary gas chromatography (GC) and synchronous spectrofluorometry (UV).

Surface sediments at both sites contain moderate concentrations (5-50  $\mu\text{g/g}$  dry weight) of weathered petrogenic and biogenic hydrocarbons. Concentrations are highly correlated with total organic carbon levels in the sediment. Hydrocarbon levels in seawater range from 6 to 80  $\mu\text{g/l}$ . Biogenic and petrogenic hydrocarbons dominate the GC traces, and two-ring aromatics dominate the UV spectra. Concentrations of total hydrocarbons in both seawater and sediment at the West Hackberry site are 2-5 times higher than those at the Weeks Island site.

White and brown shrimp contain low concentrations of hydrocarbons (5-90  $\mu\text{g/g}$  dry weight) at both sites. Epibenthic fauna (crabs) contain much higher concentrations of hydrocarbons (30-70  $\mu\text{g/g}$  dry weight). This difference may be attributable to feeding behavior of different species.

Recommendations for environmental indicators and monitoring techniques are made.

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## 1. Introduction

### 1.1 Purpose of the Study

Marine ecosystems are stabilized by fluxes of nutrients and essential elements between the various compartments composing the system. Monitoring the health of the ecosystem following offshore development requires that marine scientists determine whether these fluxes and those of potentially toxic chemicals produced during this development are changing. To conduct an efficient and revealing monitoring program requires that the system be defined prior to its possible perturbation (i.e., the establishment of the environmental baseline) and that the best possible methods for monitoring changes be developed.

As part of an interdisciplinary scientific effort to provide baseline oceanographic data for estimating environmental effects caused by discharging possibly contaminated, highly saline water into coastal waters, we have undertaken a field and laboratory analysis program to examine hydrocarbon distributions in the marine environment at two sites off the coast of Louisiana. The offshore West Hackberry and Weeks Island brine diffuser sites, two of the proposed sites at which brine from salt dome leaching (cavitation) operations of the DOE Strategic Petroleum reserve project will be pumped, were the focuses of this study.

Our goals during this study were threefold:

1. To describe the present levels and sources of hydrocarbon compounds in whole seawater, surface sediment and selected marine biota at stations centered around each site.

2. To examine the temporal (seasonal) variations of these measurements at each site.
3. To evaluate several different analytical techniques for their efficiency in describing the chemical environment and their use in monitoring activities.

## 1.2 Literature Survey

A variety of published and unpublished studies have been undertaken during the past decade which focused on ambient levels of hydrocarbons in the Gulf of Mexico continental shelf environment. Examples of such studies are presented in Table 1 although this list is by no means complete. One basic conclusion from the combined results of these studies is that the nearshore environment of the Gulf is a complex, largely heterogeneous environment with respect to oceanographic and sedimentological regimes. The Mississippi River drainage has a profound influence on the entire Gulf and directly affects the marine environment "downstream" to the west. Local inputs from other riverine and estuarine systems (e.g. Atchafalaya River) definitely influence waters with which they couple on the shelf from aspects of land runoff and accompanying pollutant and normal sediment inputs. Thus, a definition of the marine environment at a particular offshore site (e.g., West Hackberry and Weeks Island offshore diffuser sites) requires focused attention on each site rather than a reliance on previous large-scale studies on the continental shelf.

The hydrocarbon chemistry of a particular offshore site is fully defined only by:

TABLE 1

GULF OF MEXICO HYDROCARBON  
CHEMISTRY STUDIES (PARTIAL LIST)

STUDY	LOCATION
Berryhill (1975)	South Texas Shelf
Middleditch & Basile (1978)	Buccaneer Oil Field - Texas Coast
Boehm (1978a)	MAFLA - Sediments
Bieri (1978)	MAFLA - Biota
Calder (1978)	MAFLA - Water column
Iliffe and Calder (1973)	Loop Current - Water column
Gearing et al. (1976)	MAFLA - Water column
Palacas et al. (1976)	Eastern Gulf - Sediments
Giam et al. (1976)	Hydrocarbons - Organisms
Parker et al. (1976)	Zooplankton, Sediment, Biota
Shokes and Paine (unpublished)	SPRO - Hydrocarbons

1. An evaluation of the absolute concentrations of total hydrocarbons (gross concentrations).
2. An evaluation of the concentrations of key individual hydrocarbon compounds.
3. An evaluation of the source(s) of the observed hydrocarbon distributions.
4. Comparisons of the concentrations and composition of a particular sample type with other sample types.
5. A consideration of how items 1 through 4 vary spatially and temporally (seasonality).

Items 1 through 5 collectively define the hydrocarbon chemistry of the site. Hydrocarbons are a class of organic compounds, and most often the "total hydrocarbons" extracted and isolated from a particular sample are composed of many different compounds (e.g., crude oils contain thousands of individual compounds while unpolluted algae and zooplankton contain only several major biosynthesized hydrocarbons). It is insufficient to describe the hydrocarbon chemistry of the environment in terms of gross concentration information alone. For example, to say that a water sample contains 450 parts per billion ( $\mu\text{g}/\text{liter}$ ) of hydrocarbons reveals nothing about the nature of the sample. The sample may be comprised of 450 ppb of a single compound, pristane, a common branched hydrocarbon of zooplanktonic origin, or may be comprised of 450 ppb of crude oil containing a thousand compounds.

The hydrocarbon composition of samples taken from the nearshore region of the Gulf of Mexico must be evaluated in terms of the various sources of hydrocarbons that may collectively determine the nature of the chemistry of the sample. The West Hackberry and Weeks Island sites upon which this study focuses are influenced by (a) Mississippi Riverine input, (b) Atchafalaya riverine input, (c) local hydrocarbon inputs from platform operations and (d) inputs of biogenic (biosynthesized) hydrocarbons. For example, Figure 1 illustrates representative gas chromatograms (glass capillary) of sediment hydrocarbon patterns characteristic of potential sources in the region compared with a crude oil. Note that in the composite chromatogram (Figure 1E) the various inputs of biogenic and petrogenic hydrocarbons can be subjectively "extracted", and one can separately evaluate the relative importance of each source in the composite sample.

This sets the stage for the full evaluation of the hydrocarbon chemistry of the four seasons of the water, sediment and biota samples fully analyzed to date. In this report, data on concentrations of hydrocarbons must be related to source material as revealed in high resolution gas chromatographic and spectrofluorometric determinations.

Four seasons of data are summarized below and interpreted. Statistical determinations on within-station variability will also be presented. This variation must be known so as to be able to determine in a monitoring study whether or not concentrations are actually changing with time. The use of glass capillary gas chromatography (GC) in conjunction with spectrofluorometry will be evaluated, and the relation of the hydrocarbon data to selected nonhydrocarbon data will be discussed.



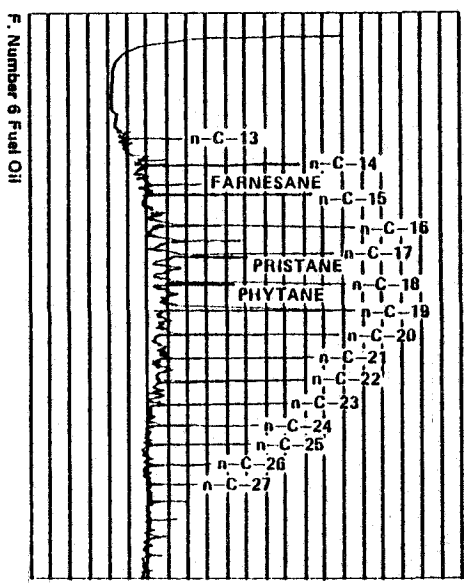
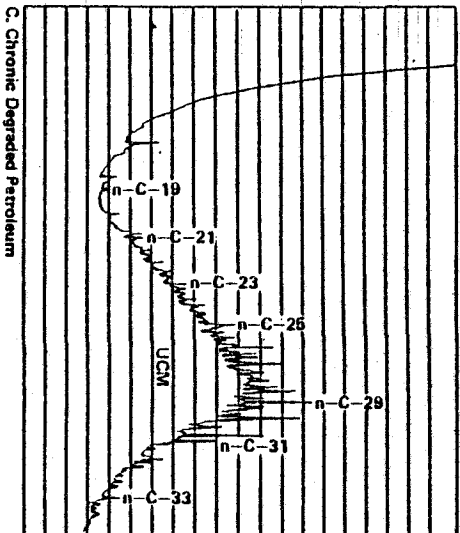
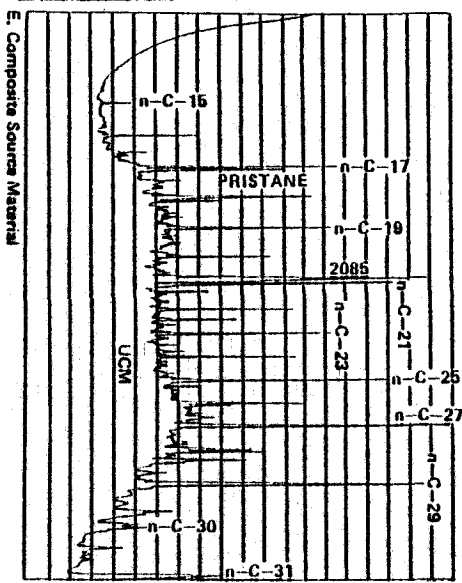
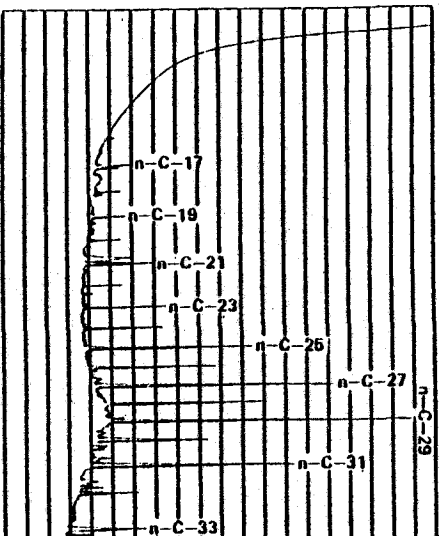
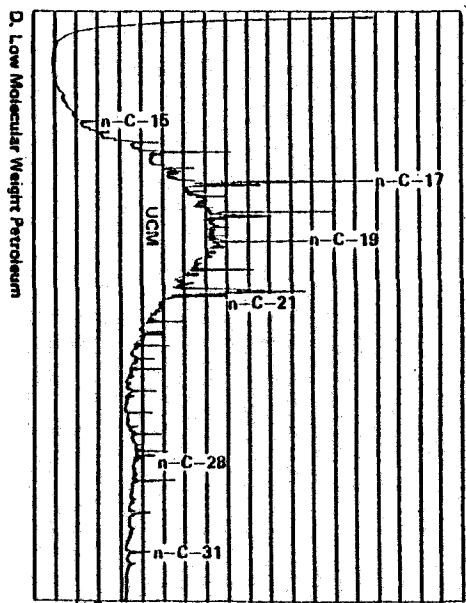
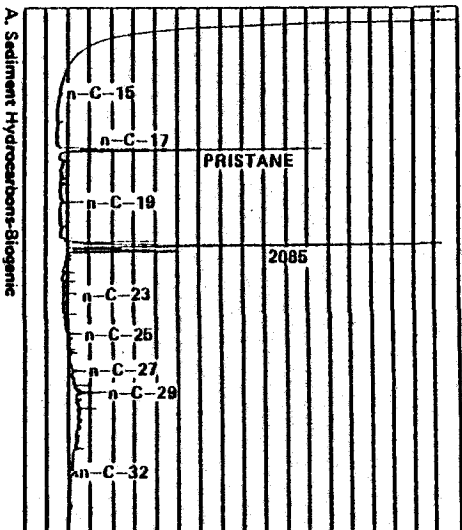


Figure 2. Gas chromatograms illustrating different sources of observed hydrocarbons.

### 1.3 Previous Work

The background chemical oceanography and biogeochemistry of the West Hackberry and Weeks Island brine disposal sites have been studied as part of the Department of Energy's Environmental Impact Statement preparation (DOE, 1978; Shokes, 1978). This study focused on limited analyses of surface sediment, filter water, fish and shrimp from the two sites. Results will be compared to those of the present study in individual sections of this report.

## 2. Methods and Materials

### 2.1 Sampling and Analytical Rationale

The sampling and analytical scheme employed in this study was designed to meet the overall program objectives within the constraints of the predetermined sampling grid, the sampling platform and the limited funding available to the project. The basic sampling approach did not include obtaining samples at all thirteen proposed stations at each site. We did not anticipate that the small-scale, predisposal chemical variations throughout the study area would warrant such a detailed and expensive hydrocarbon chemistry sampling grid. The sampling design did include seasonal sampling at the same five stations in all four seasons and emphasized the measurement of the statistical variability of the hydrocarbon analyses for all sample types. Wherever possible, replicate samples were collected at a single station, composited and analyzed as a single sample. In this way, the statistical reliability of the analyses was improved without dramatically increasing the analytical costs as would result if replicates were analyzed at each station for each sampling period.

Each sample was analyzed by two complementary techniques: ultra-violet/spectrofluorometry and high resolution gas chromatography. Both analyses were performed on a combined  $f_1$  and  $f_2$  fraction of the sample extract. Since the long-term objective of the Strategic Petroleum Reserve Monitoring program was to develop a monitoring scheme for the ecosystem in the vicinity of the brine diffuser sites, and not simply to provide a detailed characterization of the region, the

information lost by combining the two fractions was more than compensated by the gain in analytical efficiency and the reduction in analytical costs.

Glass capillary gas chromatography of the combined  $f_1$  and  $f_2$  fractions provided information about the concentrations of individual hydrocarbon components present in the samples. From the chromatogram, changes in the hydrocarbon fingerprint can be selected which are indicative of an additional input of hydrocarbons not evident from measurements of total hydrocarbon concentrations (Ehrhardt and Blumer, 1972). Changes in the biogenic hydrocarbon composition of the samples resulting from a change in either the source material or transport mechanisms in the vicinity of the site can also be determined.

Spectrofluorometry was used to characterize and quantify the aromatic and heterocyclic compounds present in the sediment extracts (Wakeham, 1977). It is a rapid and inexpensive technique for screening sediment samples; its true value may be as a rapid and inexpensive monitoring tool. Spectrofluorometry has the advantage of being selectively sensitive to aromatic hydrocarbons and insensitive to most biogenic hydrocarbons. Because of this feature, small inputs of aromatic hydrocarbons to the ecosystem can be easily monitored. The technique is particularly appropriate for a brine monitoring program since the predominant and most toxic organic components of the brine discharge will most likely be the aromatic hydrocarbons.

## 2.2 Sampling

### 2.2.1 Station Locations

The general location of the sampling sites and the sampling grid for the West Hackberry (Texoma) and Weeks Island (Capline) sites are presented in Figure 2. A summary of exact station locations and types of samples taken at each station are presented in Table 2. The hydrocarbon chemistry sampling grid is a subset of the entire program sampling grid. We selected the number of sites for sampling that would address issues of spatial heterogeneity for each type of sample collected within the overall resources of the project. Sediment, epifaunal and water column samplings were conducted along the approximate east-west transect through the diffuser site. However, macrofauna (shrimp) were sampled at three sites only, due to their mobility throughout the entire sampling grid.

### 2.2.2 Sample Collection

Three types of samples - bottom sediments, macrocrustaceans and whole seawater samples - were collected and analyzed under the scope of the hydrocarbon work unit.

Strict precautions were taken to ensure that the samples were both representative of the sample population and not contaminated from shipboard sources of hydrocarbons. Bottom sediments were collected with a stainless steel modified Van Veen grab sampler, shrimp with a semi-balloon trawl fitted with 1-3/4" untarred nylon nets, and whole seawater with a 10-liter Teflon-lined Go-Flo seawater sampler. Either nylon- or polymer-coated wires were used to deploy the sampling gear.

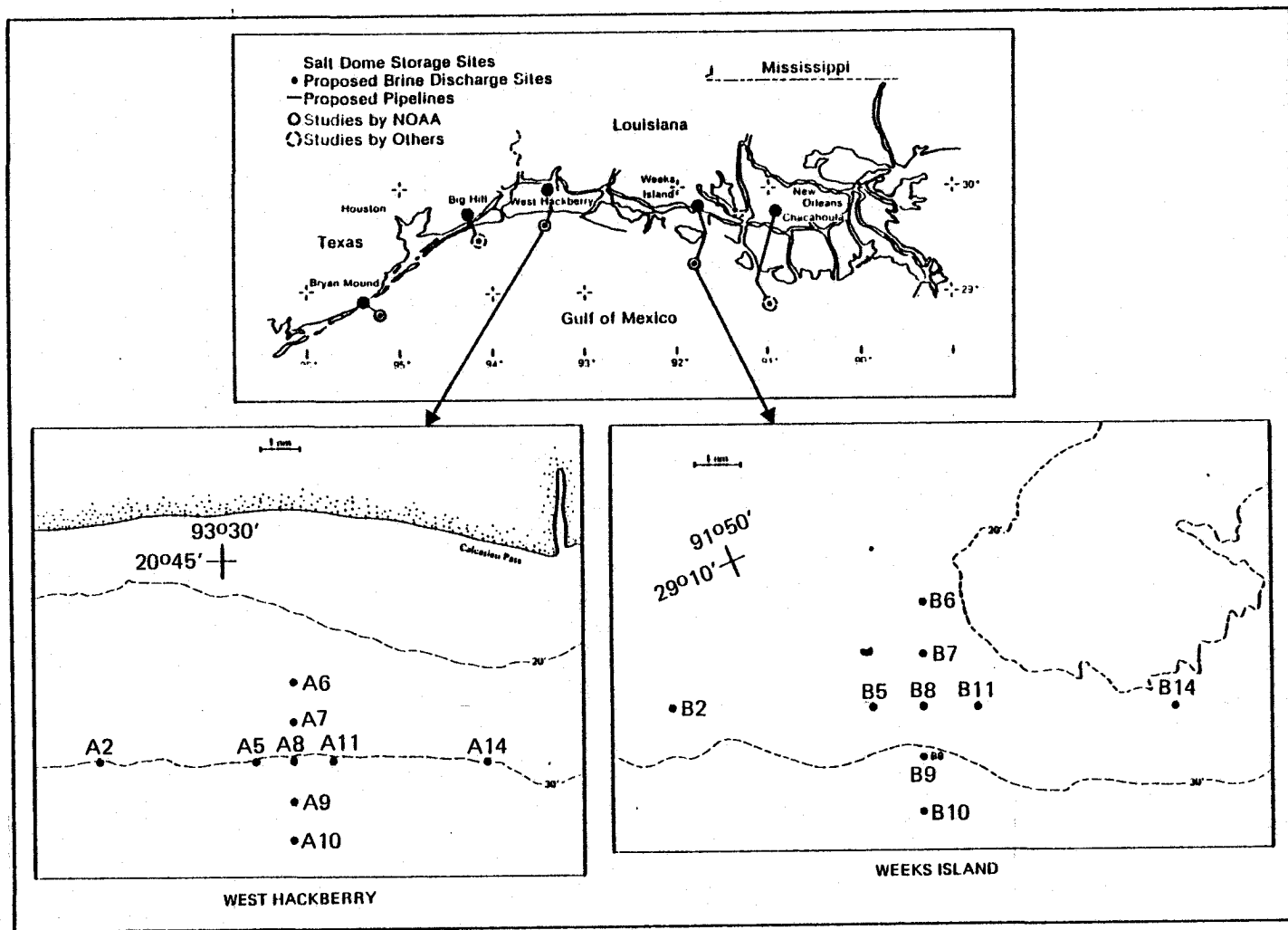


Figure 1. Location of study areas & station locations.

TABLE 2

STATION LOCATIONS AND SAMPLING STRATEGY<sup>a</sup>

SITE	STATION	LOCATION		SAMPLES COLLECTED
		LAT.	LONG.	
West Hackberry	A2	29°39.76'N	93°33.78'W	SW, S, E, M
	A5	39.90	29.16'	SW, S, E
	A8	40.00	28.00'	SW, S, E, M
	A11	40.06	26.90'	SW, S, E
	A14	40.33	22.29'	SW, S, E
	A10	38.00'	27.86'	M
Weeks Island	B2	29°07.07'	91°52.71'	SW, S, E, M
	B5	06.15'	48.62'	SW, S, E
	B8	05.70'	47.60	SW, S, E, M
	B11	05.28'	46.54'	SW, S, E
	B14	03.43'	42.21'	SW, S, E
	B10	03.91'	43.50'	M

<sup>a</sup>KEY:

SW = Whole seawater

S = Sediment

E = Epifauna (snails, crabs)

M = Macrofauna (shrimp)

The vessel was positioned so that smokestack emissions were not carried across the sampling platform during sampling operations. All sub-sampling was accomplished using solvent-rinsed stainless steel, Teflon or glass implements.

Bottom sediment samples were collected by removing the top 3 cm of sediment from the grab sample with a solvent-rinsed Teflon spatula. Equal portions of material from four successive grabs were combined in a solvent-rinsed Teflon container and frozen at  $-10^{\circ}$  C immediately after collection. In the laboratory, the sediment sample was thawed, homogenized, split into subsamples for various chemical analyses (hydrocarbon, trace metal, total organic carbon, and grain size analyses), refrozen, and stored at  $-10^{\circ}$  C awaiting analysis.

The entire seawater sample (unfiltered) was drained from the sampler through silicone-rubber tubing into solvent-rinsed 20-liter glass carboys, preserved with 100 ml of dichloromethane ( $\text{CH}_2\text{Cl}_2$ , Baker Resi-Analyzed), capped and stored prior to extraction.

The contents of the trawl net were emptied into a clean aluminum container. Twenty to thirty individuals of the appropriate species were selected with solvent-rinsed metal tongs, placed in a solvent-rinsed glass jar, and frozen at  $-10^{\circ}$  C immediately after collection. Care was taken to collect individuals of a single species. Species identifications were made with the help of the marine biologists participating in the field sampling effort.



## 2.3 Analytical Chemistry

### 2.3.1 Sample Processing

The unfiltered seawater samples were processed by a combination of field and laboratory procedures (Figure 3). The seawater samples were extracted on board within 6 hours of collection by turbulently stirring 250 ml of  $\text{CH}_2\text{Cl}_2$  with the 10 liters of seawater for 15 minutes with a high-speed electric stirrer (Talboy's Engineering Model 101). The two phases were allowed to separate for 10 minutes and the solvent extract siphoned with a stainless-steel tube, a glass filter flask and a hand vacuum pump. The process was repeated two additional times to ensure high extraction efficiency (95 percent as determined in laboratory spiking experiments). The three extracts were combined in a 1-liter glass bottle with a Teflon-lined cap and stored in the dark at ambient temperatures.

In the laboratory, the dichloromethane extracts were dried with sodium sulfate ( $\text{Na}_2\text{SO}_4$ , Baker-Analyzed) and concentrated to 100 ml using rotary evaporation and evaporation under a purified nitrogen stream. Dichloromethane was displaced with hexane and an aliquot weighed on a Cahn Model 28 electrobalance. The samples were then fractionated by column chromatography and analyzed as discussed below.

Benthic organism samples were extracted with the method of Boehm and Quinn, 1978 (Figure 4). After the sample was thawed and weighed, a small portion of tissue was removed for a wet weight/dry weight determination. The remaining sample and 100 ml of methanol ( $\text{CH}_3\text{OH}$ , Baker Resi-Analyzed) were added to a Waring blender and homogenized for 60 seconds. The homogenate and 50 ml of 0.5 N aqueous potassium

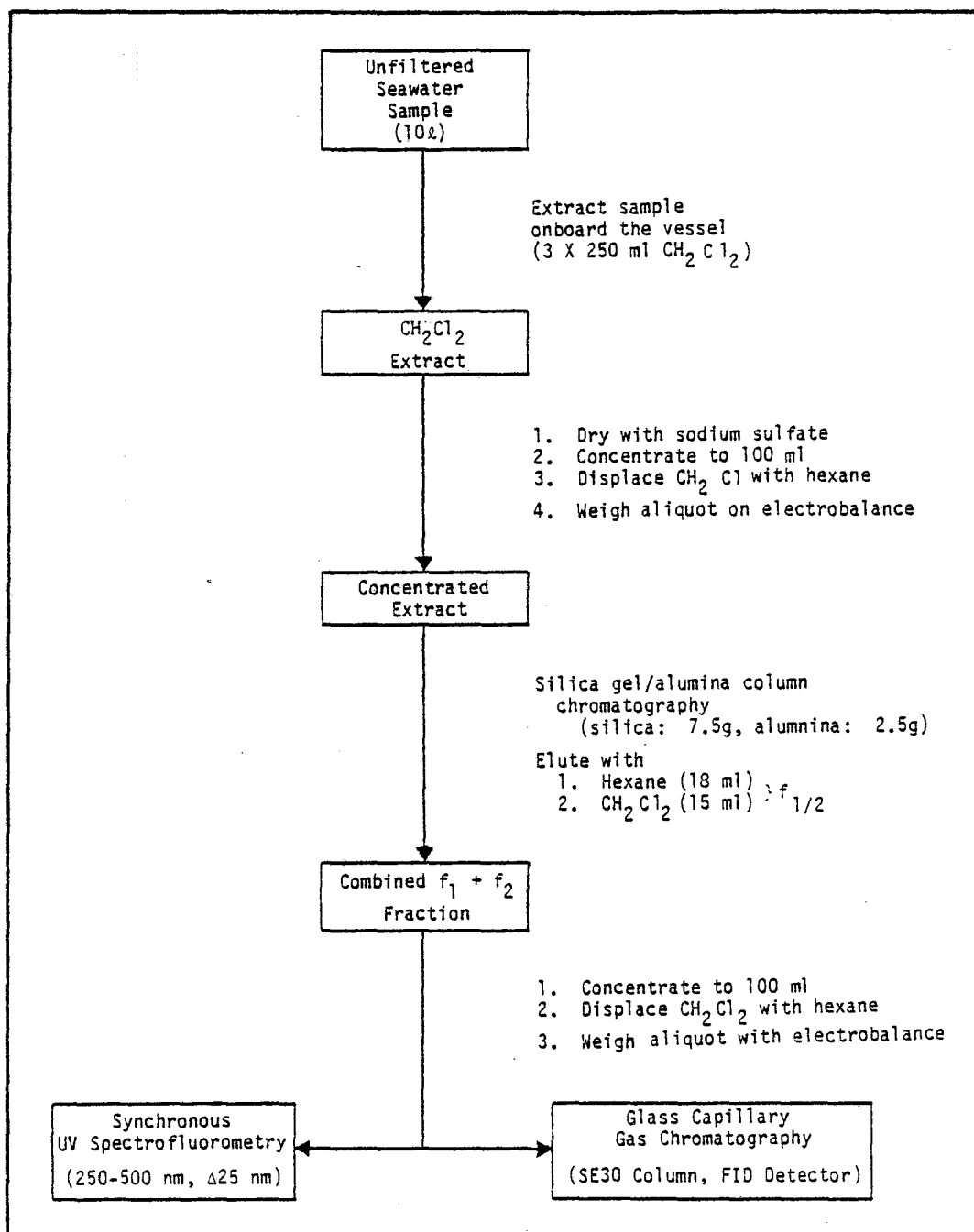


Figure 3. Analytical scheme for seawater samples.

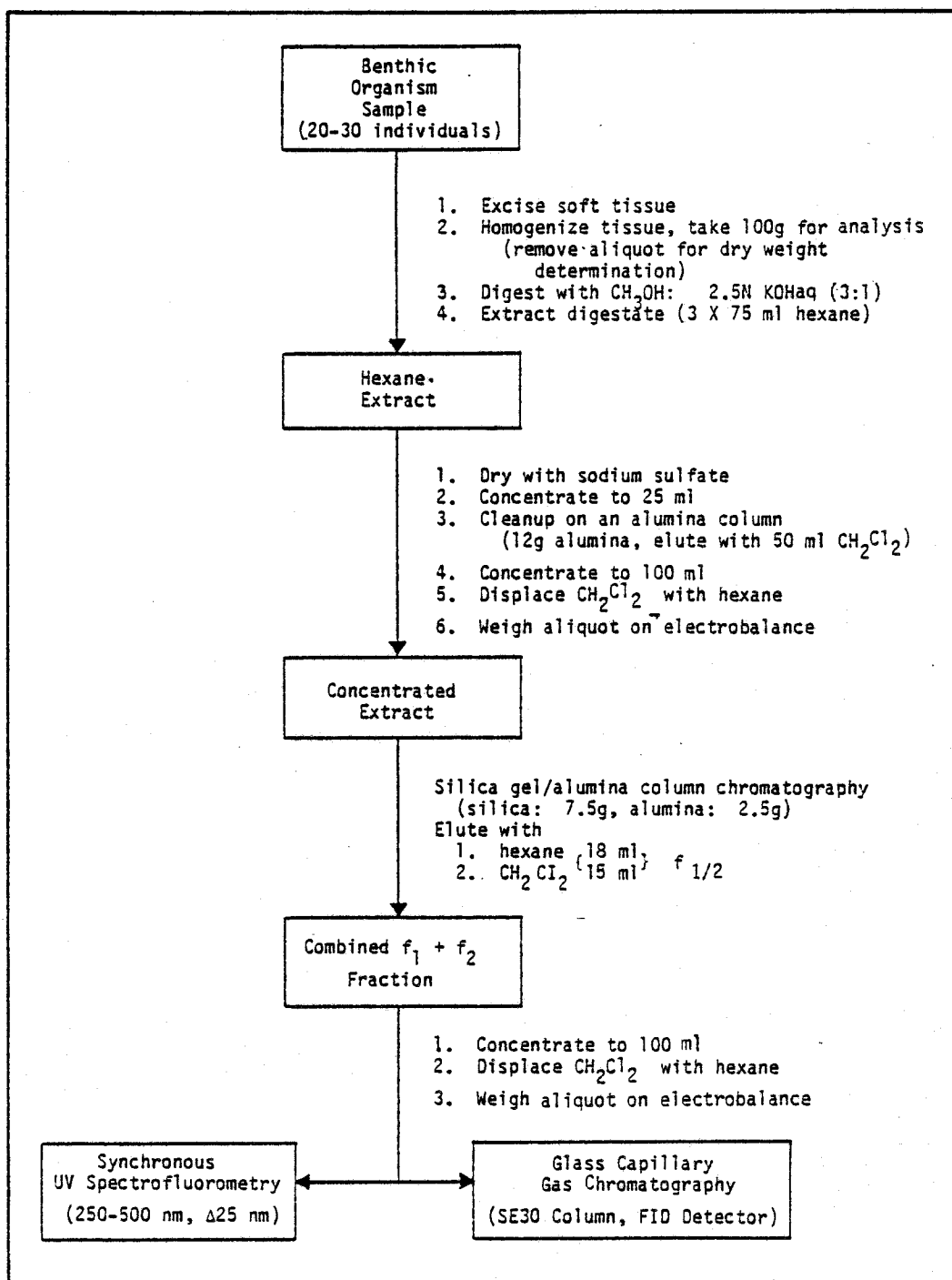


Figure 4. Analytical scheme for benthic organism samples.

hydroxide (KOH, Baker-analyzed) were digested for 4 hours in a 1-liter flask, added to a separatory funnel containing 100 ml of saturated aqueous sodium chloride (NaCl, Baker-analyzed) and extracted three times with 75 ml of hexane (Baker, Resi-Analyzed). The extract was dried over anhydrous sodium sulfate and rotary evaporated to approximately 1 ml. To remove the hexane soluble gelatinous material at this point, the samples were transferred to an alumina column (12 g, 5 percent water deactivated) and eluted with 50 ml of  $\text{CH}_2\text{Cl}_2$ . The column retains hexane soluble, high molecular weight biogenic lipids which interfere with the column chromatography fractionation procedure. The dichloromethane extracts were concentrated to 100 ml using rotary evaporation and then to near dryness under a purified nitrogen stream. Dichloromethane was displaced with hexane and an aliquot weighed on a Cahn Model 28 electrobalance. The samples were then fractionated by column chromatography and analyzed as discussed below.

Bottom sediment samples were extracted using the method of Boehm and Quinn, 1978 (Figure 5). The thawed sample was homogenized and a 100-g aliquot weighed into a 500-ml flask. After the addition of 300 ml of methanol/toluene (7:3) (toluene, Baker Resi-Analyzed) and 50 ml of 2.5 N aqueous KOH (final concentration 0.5 N KOH/methanol/aqueous) the mixture was refluxed for four hours. The extraction mixture was vacuum filtered with a precombusted glass fiber filter (Whatman GF/A) and a Buchner funnel. The filtrate was added to a separatory funnel containing 50 ml of distilled water, extracted three times with 50 ml of hexane and dried over sodium sulfate. The hexane extract was concentrated to 100 ml using rotary evaporation and

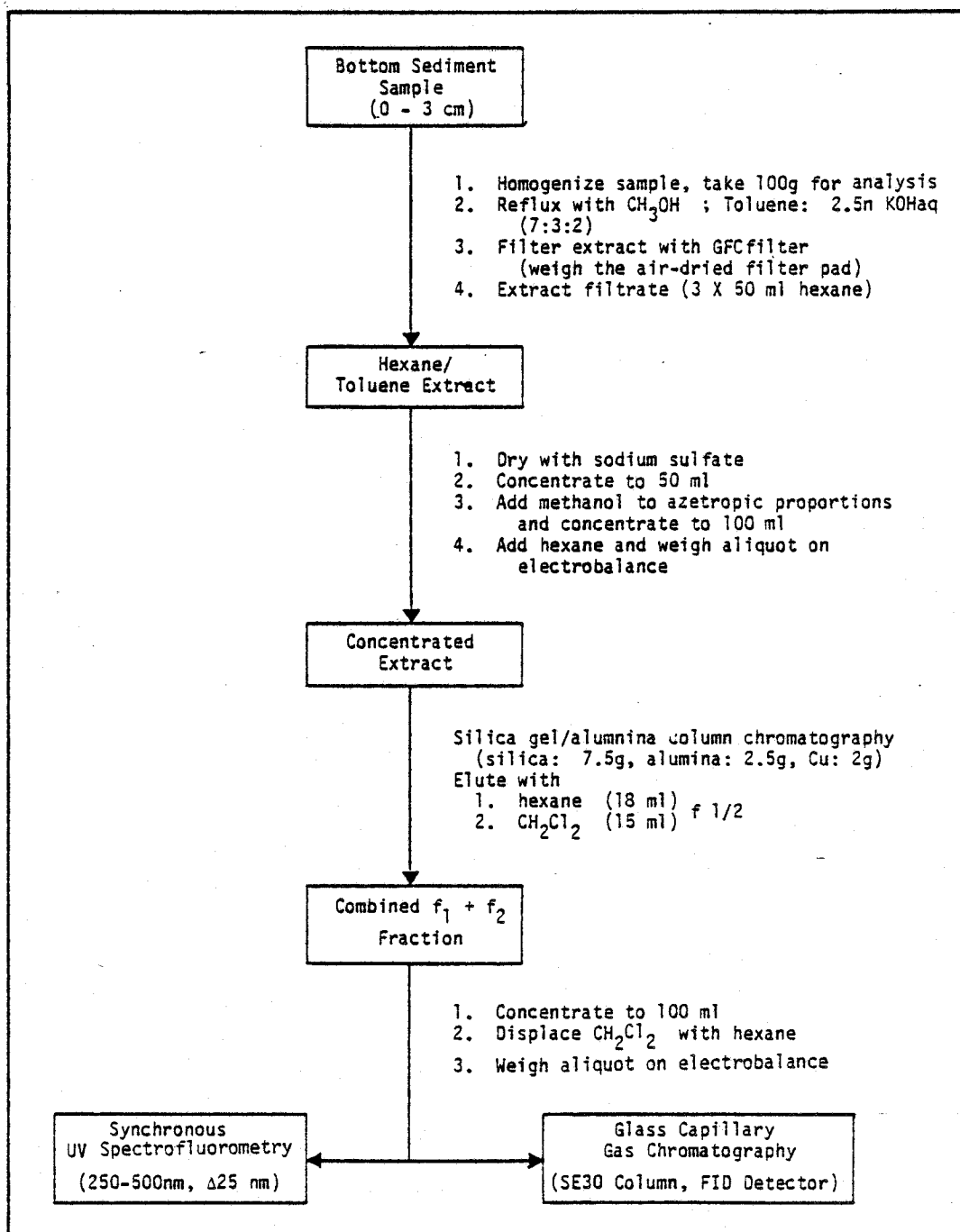


Figure 5. Analytical scheme for bottom sediment samples.

evaporation under a purified nitrogen stream. An aliquot of the extract was weighed on a Cahn Model 28 electrobalance. The samples were then fractionated by column chromatography and analyzed as discussed below. The filter cake was dried at 45° C for 16 hours, and weighed to measure the dry weight of the extracted sediment.

The sample extracts from all three sample types - whole seawater, benthic organisms, and bottom sediments - are handled similarly following the extraction steps. The dried extract is reduced in volume to 1 ml on a rotary evaporator and transferred to a silica gel/alumina column for column chromatography. The column, which consists of 7.5 g silica gel (100 percent activated), 2.5 g of alumina (5 percent activated), and 2 g of activated copper metal powder (rinsed with 10 percent HCl, water, and methanol), is wet-packed in CH<sub>2</sub>Cl<sub>2</sub> and eluted with 30 ml each of CH<sub>2</sub>Cl<sub>2</sub> and hexane to clean it. The column is eluted with 18 ml of hexane (fraction 1), then 15 ml of dichloromethane (fraction 2), which are combined in a single fraction, f<sub>1/2</sub>, containing saturated, unsaturated and aromatic hydrocarbons.

The fraction is evaporated almost to dryness, transferred to a graduated centrifuge tube, and diluted with hexane to a known volume. One aliquot is evaporated and weighed on a Cahn electrobalance for a gravimetric measurement of total hydrocarbons. A second aliquot is used for analysis by spectrofluorometry, and the remainder is transferred to a glass sample vial, evaporated under a stream of nitrogen and analyzed by glass capillary gas chromatography.

### 2.3.2 Sample Analysis

The  $f_{1/2}$  fractions of the sample extracts were analyzed by three complementary techniques: gravimetric analysis, synchronous spectrofluorometry, and glass capillary gas chromatography. The gravimetric analysis consists of taking a known aliquot from a known volume of hexane in which the fraction is dissolved, evaporating the solvent on a tared aluminum pan and weighing the residue on a Cahn Model 28 electrobalance. Two or three replicate analyses are averaged to obtain the gravimetric determination. The technique measures the total nonvolatile hydrocarbons present in the fraction.

The fluorescence spectra of the sample extracts were measured using the synchronous fluorescence spectroscopy technique of Wakeham (1977). In summary, a measured aliquot of the sample was dissolved in a known volume of hexane. The intensity of the fluorescence emission was measured from a wavelength from 250 nm to 500 nm while synchronously scanning the excitation wavelength 25 nm shorter than the wavelength at which the emission was measured. The analysis was done on a Farrand Mark I spectrofluorometer equipped with corrected excitation and emission modules and a dual beam sample cell. The corrected measurement technique makes data taken at different times and on different instruments intercomparable. The dual beam option allows any background signal contributed by the solvent to be subtracted.

Major peaks of the fluorescence spectra were quantified on a sample weight or sample volume basis. Daily changes in instrumental sensitivity were measured by analyzing a series of standards containing various amounts of No. 2 fuel oil. One of each sample type was analyzed

at several concentrations to ensure that the sample was dilute enough to eliminate spectral distortions caused by inner filter effects (Parker, 1969).

The intensity of the fluorescence spectra was measured at each of several wavelengths which correspond to peak maxima common to a given sample type. The peak heights were converted to concentration units by using a reference oil with spectral characteristics similar to the sample spectra. No. 2 fuel (API Reference No. 2) was used as a standard for the seawater and organism samples and Bunker C oil (API Reference No. 4) for the bottom sediment samples. Perylene (Aldrich, 99+ percent gold label) was used to quantify the 438-nm peak which was common to the spectra of the bottom sediment samples. The wavelengths at which the peak height was measured and the response factors used for the calculations are summarized by sample type in Table 3.

High resolution glass capillary gas chromatography (GC) was used to characterize and quantify the major hydrocarbons present in the samples. A small portion of the sample was injected into a Hewlett-Packard 5840A gas chromatograph equipped with either a 15-meter or 30-meter SE-30 WCOT column (J&W Scientific) and a flame ionization detector (FID). The run was temperature programmed from 60° C to 260° C at 3° C/minute. The area of individual peaks was electronically integrated and converted to a concentration based on the detector response of a known amount of internal standard (androstane) added to each sample during the extraction step. The area of the unresolved envelope was measured by planimetry and converted to a concentration using a measured conversion factor between planimeter units and



TABLE 3

WAVELENGTHS AND RESPONSE FACTORS  
FOR THE SPECTROFLUOROMETRY CALCULATIONS

SAMPLE TYPE	WAVELENGTH (nm)	RESPONSE FACTOR <sup>a</sup>
Seawater	288	1.0
	312	1.0
	328	1.0
	348	1.0
	405	1.0
Organism	310	1.0
	325	1.0
	348	1.0
Bottom Sediment	312	2.0
	327	2.0
	342	2.0
	405	2.0
	438	0.0075

<sup>a</sup> Response factor relative to No. 2 fuel oil (API Reference No. 2) where Concentration = Factor x Nominal concentration

integrator units. Retention indices of individual peaks were calculated using the retention times of n-alkanes from n-C<sub>10</sub> to n-C<sub>34</sub> in a hydrocarbon standard which was analyzed daily.

The high resolution glass capillary columns resolve a large number of hydrocarbon peaks in each sample. Although retention indices and concentrations of each peak are calculated and stored by the data processing computer, only selected major peaks are reported on the data forms. These peaks have been chosen either as marker compounds representative of an environmental source of hydrocarbons or as a major peak common to a group of samples. The retention indices of the reported peaks are summarized by sample type in Table 4. The concentration of the unresolved complex mixture of hydrocarbons composing the unresolved envelope is reported and is necessary for the proper interpretation of the hydrocarbon composition of environmental samples. Hydrocarbon concentrations are available either as determined gravimetrically or by GC/sum of resolved and unresolved parts of the GC trace.

TABLE 4

RETENTION INDICES OF REPORTED PEAKS FOR  
THE GLASS CAPILLARY GAS CHROMATOGRAPHIC ANALYSIS

SAMPLE TYPE	RETENTION INDEX <sup>a</sup>	COMPOUND NAME
Seawater	1300	nC13
	1500	nC15
	1708	Pristane
	2028	Heneicosahexaene (polyolefin)
	2800	nC28 + squalene
	2900	nC29
Organism	1500	nC15
	1708	Pristane
	2800	nC28 + squalene
	2900	nC29
Bottom Sediment	1500	nC15
	1708	Pristane
	2086	Cycloolefin <sup>b</sup>
	2800	nC28 + squalene
	2900	nC29

<sup>a</sup>Retention indices on a 15-meter SE-30 glass capillary column temperature programmed from 60° to 275° C at 3° C/minute.

<sup>b</sup>Boehm and Quinn, 1978; Gearing et al., 1976.

### 3. Results

#### 3.1 Seawater

As mentioned previously, whole seawater samples were extracted on board the sampling ship. Separation into dissolved and particulate fractions was not attempted in this study; therefore, the results are not directly comparable with those of Shokes (1977) or DOE (1978) where dissolved hydrocarbons were measured.

Brine disposal operations may lead to the introduction of water-soluble oil and/or oil dispersions into the water column once dome filling and refilling operations are begun. These hydrocarbons may adsorb to particles in the water column. Coupling between the water column and surface sediment (i.e., transport between the two reservoirs) occurs mainly through the particulate phase in the water column (Boehm, 1979), while hydrocarbon uptake by filter feeding organisms occurs mainly through the dissolved phase (non-adsorbed) (Anderson, 1978). In areas of high particulate loadings (e.g., Louisiana Continental Shelf), the hydrocarbons in the particulate phase will be many times the levels in the dissolved phase. Dissolved hydrocarbons have been observed in the 0.2 to 3 ppb level in the region. Concentrations of total water column hydrocarbons are much higher (5-20 times) than in the dissolved fraction alone (see below).

##### 3.1.1 Hydrocarbon Concentrations

Seawater hydrocarbon concentrations and composition (see next section) reflect whole seawater samples. Concentrations obtained gravimetrically for the total (aliphatic plus aromatic) hydrocarbon levels are shown in Figure 6 for the West Hackberry site and Figure 7 for the Weeks Island site, for the entire year. Variations within each

site are tabulated in Table 5, and concentration levels throughout the year can be compared. It should be stressed that absolute concentration levels by themselves do not indicate compositional differences between samples on sites. As will be seen in the next section, for example, the composition as revealed by gas chromatography indicates a drastic change in source material between the fall and winter samples at the Weeks Island site, yet the gross concentration levels are similar.

Nevertheless, the concentration data indicate that the hydrocarbon levels at the West Hackberry site are 2-3 times higher than those at Weeks Island during all seasons except spring. These differences may be due to differences in the release of petroleum from nearby oil platforms, in the amount of ship traffic or in urban inputs of petroleum to the sites. Area-wide riverine runoff during this season may obscure concentration differences between the two sites. Moreover, concentrations within the West Hackberry site are more patchy than at Weeks Island during the first two seasons with coefficients of variation ( $\sigma/\bar{x}$ ) being 0.91, 1.10 at West Hackberry and 0.29, 0.10 at Weeks Island. Between-station variability is roughly equivalent at the West Hackberry site during the winter and spring samples (0.57 and 0.50) and increases during the spring cruise at Weeks Island (0.60 in winter; 0.81 in spring). Surprisingly, the water column hydrocarbon concentrations are not related to the absolute quantity of suspended particulate matter which is comparable at both sites during all seasons at stations sampled for hydrocarbons. The best current explanation for the consistently higher seawater hydrocarbon values at West Hackberry is that the

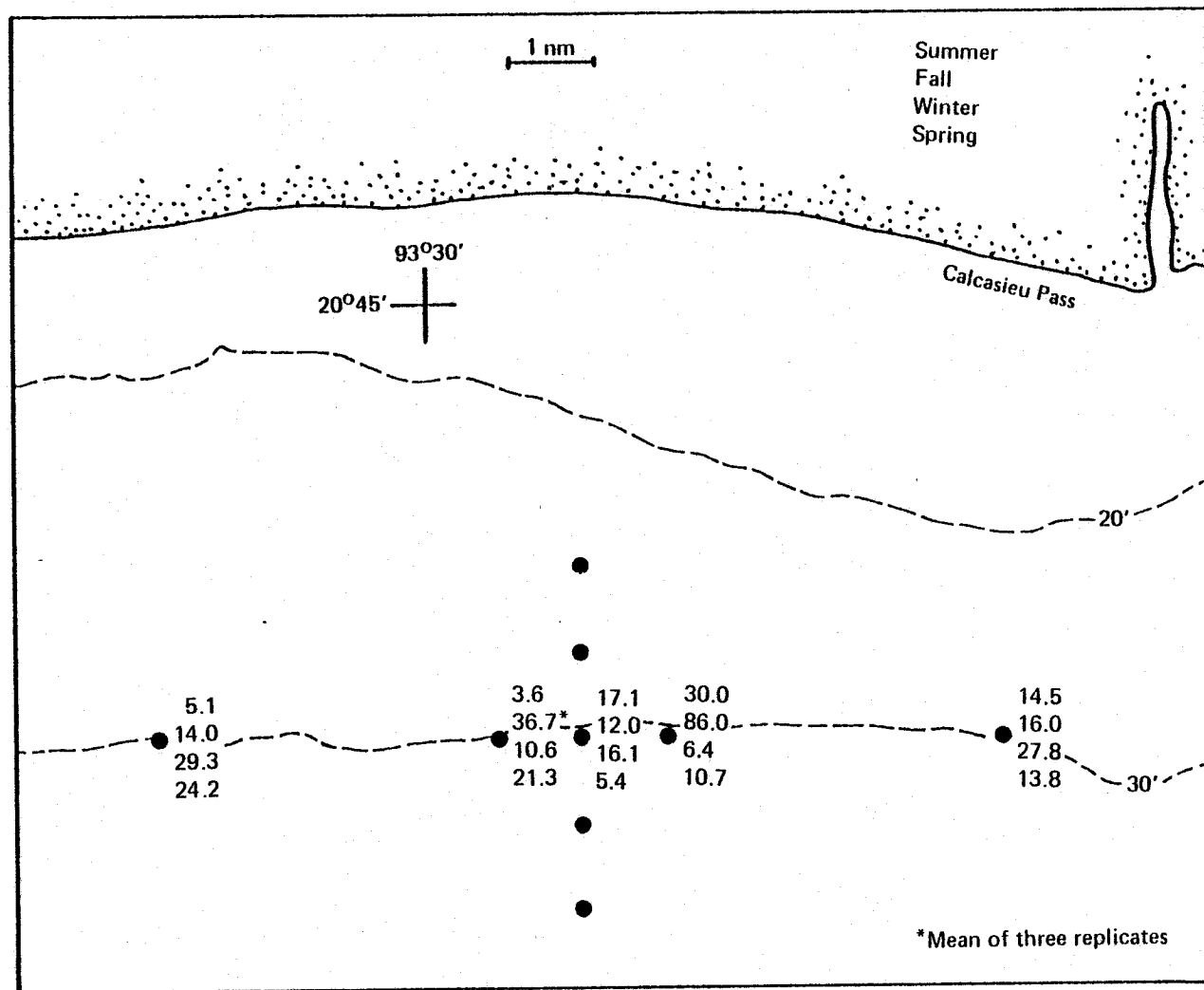


Figure 6. Hydrocarbon Concentrations in seawater samples, West Hackberry ( $\mu\text{g/liter}$ ).

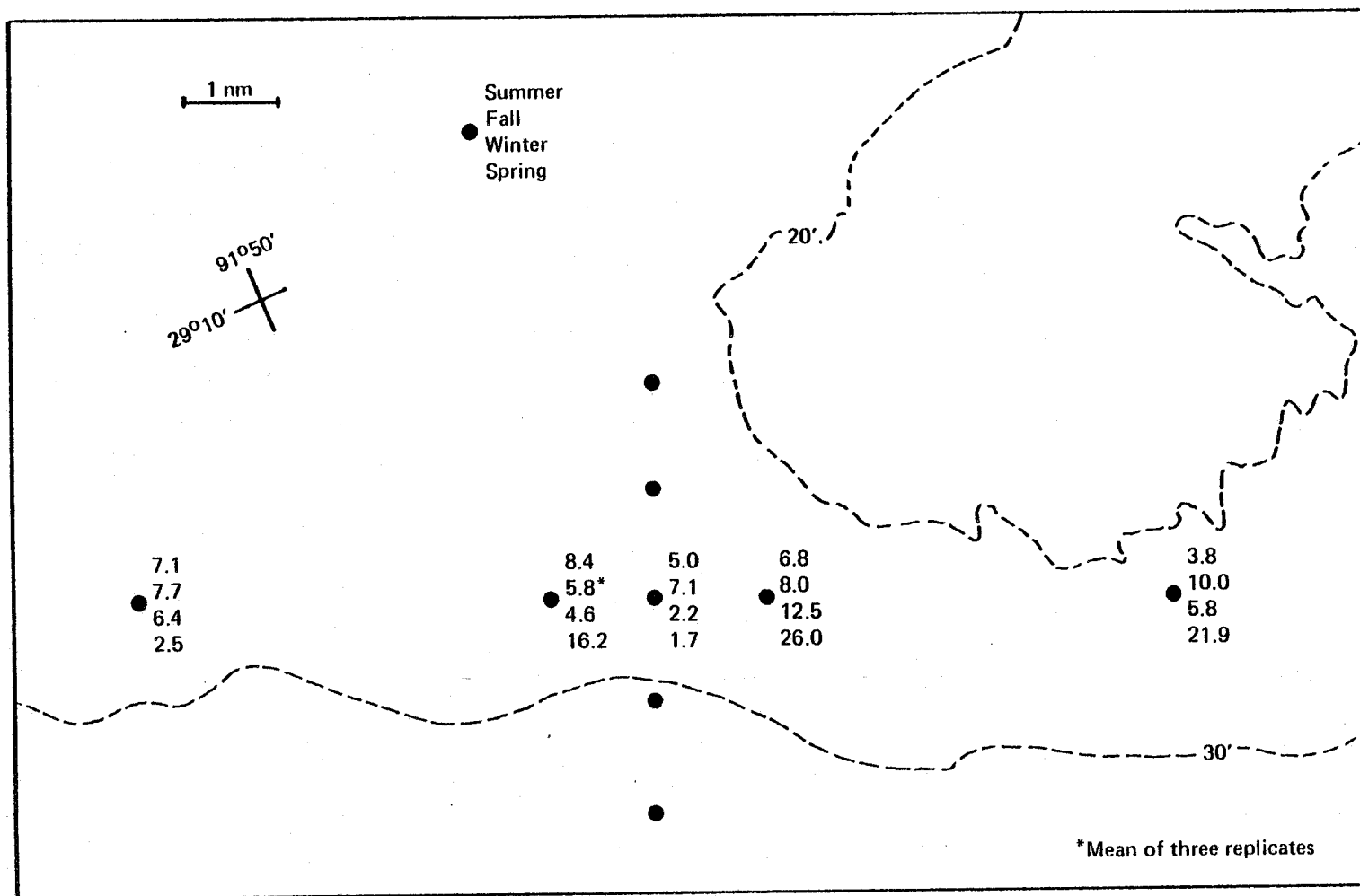


Figure 7. Hydrocarbon Concentrations in seawater samples, Weeks Island (µg/liter).

TABLE 5

SEAWATER HYDROCARBON CONCENTRATIONS BY SITE

SITE	SUMMER	FALL	WINTER	SPRING	YEAR
West Hackberry	13.3+ <u>12.1</u>	29.0+ <u>31.9</u>	18.0+ <u>10.2</u>	15.1+ <u>7.7</u>	19.0+ <u>17.6</u>
Weeks Island	6.2+ <u>1.8</u>	7.7+ <u>1.5</u>	6.3+ <u>3.8</u>	13.7+ <u>11.1</u>	8.5+ <u>6.3</u>



nearshore circulation at West Hackberry differs from that at Weeks Island and the West Hackberry site is more influenced by local (Calcasieu and/or Sabine systems) rather than regional (Mississippi) factors.

Three replicate seawater samples were obtained at stations A5 and B5 during the fall sampling to determine within-station variability. At West Hackberry, the results were 18.0, 16.0, 76.0  $\mu\text{g/l}$  ( $\bar{x}$  =  $36.7 \pm 34.1$   $\mu\text{g/l}$ ) or a coefficient of variation of 0.93. The qualitative nature of the samples (GC) indicated that no petroleum contamination from the ship was involved, so a high degree of patchiness occurred at West Hackberry. On the other hand, the water column at the Weeks Island site appears to be more uniform at a given station. Results of the three replicates were 5.3, 5.8 and 6.2  $\text{g/l}$  ( $\bar{x}$  =  $5.8 \pm 0.45$   $\text{g/l}$ ) (coefficient of variation = 0.08.)

### 3.1.2 Hydrocarbon Compositions

#### 3.1.2.1 Hydrocarbon Sources - Composition (GC)

The sources of the water column hydrocarbons observed by glass capillary gas chromatography can be classified into several categories as follows:

- B: largely biogenic (i.e., biosynthesized by marine organisms)  
n-C<sub>15</sub>, olefins, polyolefins (squalene).
- HP: high molecular weight petroleum similar to paraffinic tar distributions as observed by Butler et al. (1973).
- U: degraded petroleum or anthropogenic input as evidenced by the presence of unresolved complex mixture - UCM, (hump).
- 2A: presence of two-ringed aromatic hydrocarbons in quantities roughly equivalent to other GC peaks.

LFP: low molecular weight fresh petroleum due to sampling contamination, i.e., leakage of fuel into water.

Most water samples analyzed conform to one or more of these source classes. Examples of these four classes are shown in Figures 8 through 11. All samples are classified with respect to the source(s) of their GC-observed hydrocarbon distributions (Table 6). Where more than one source was observed in the GC profile a composite representation (e.g., HP/B) is indicated in Table 6.

Several aspects of the GC data deserve note. Most samples are composed of at least two different sources of hydrocarbons. Such a composite distribution is noted in Figure 8. The prominent presence of naphthalene compounds on the GC traces (two-ringed aromatics) is noted in about one-half of the samples. It will be seen in the next section, on UV-spectrofluorometry, that these compounds are present in all water samples to some extent. Samples were not separated into aliphatic and aromatic fractions by column chromatography. Had time and resources allowed, a more detailed distribution of aromatic hydrocarbons would have been attainable through such separation and gas chromatographic analyses of both fractions.

Throughout the two study sites, small scale heterogeneity is noted where a petroleum-related distribution is observed at one station and a biogenic distribution observed at an adjacent station. Patchiness of this sort is common to nearshore regions.

The HP distribution is much diminished during the spring sampling, although present at several of the Weeks Island and West Hackberry stations. The spring composition is largely of a biogenic origin

Seawater Hydrocarbons  
Summer Cruise (01)  
Station B5—Weeks Island

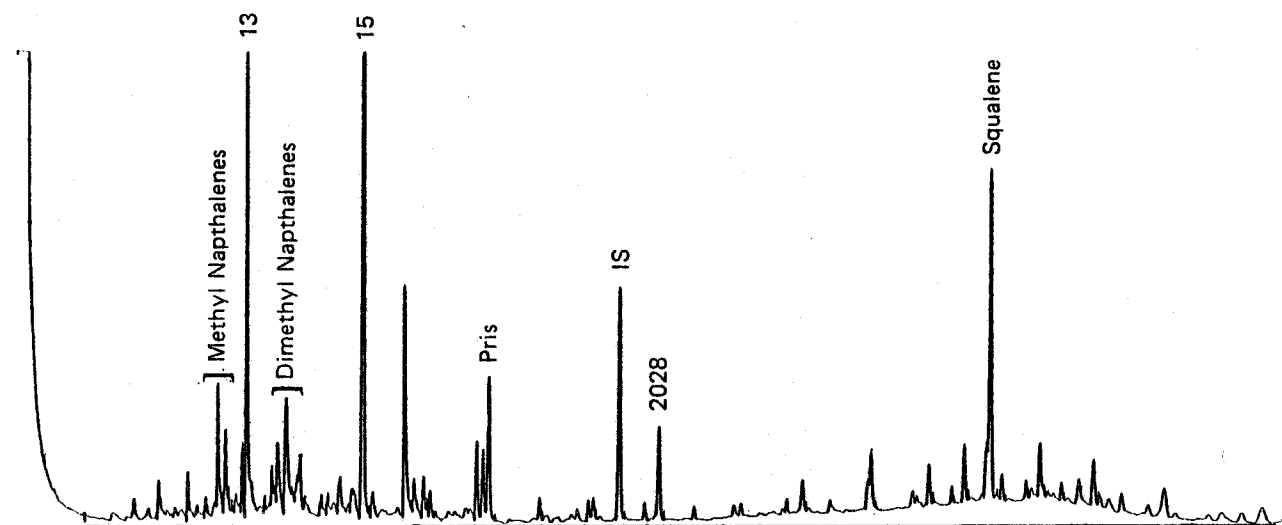
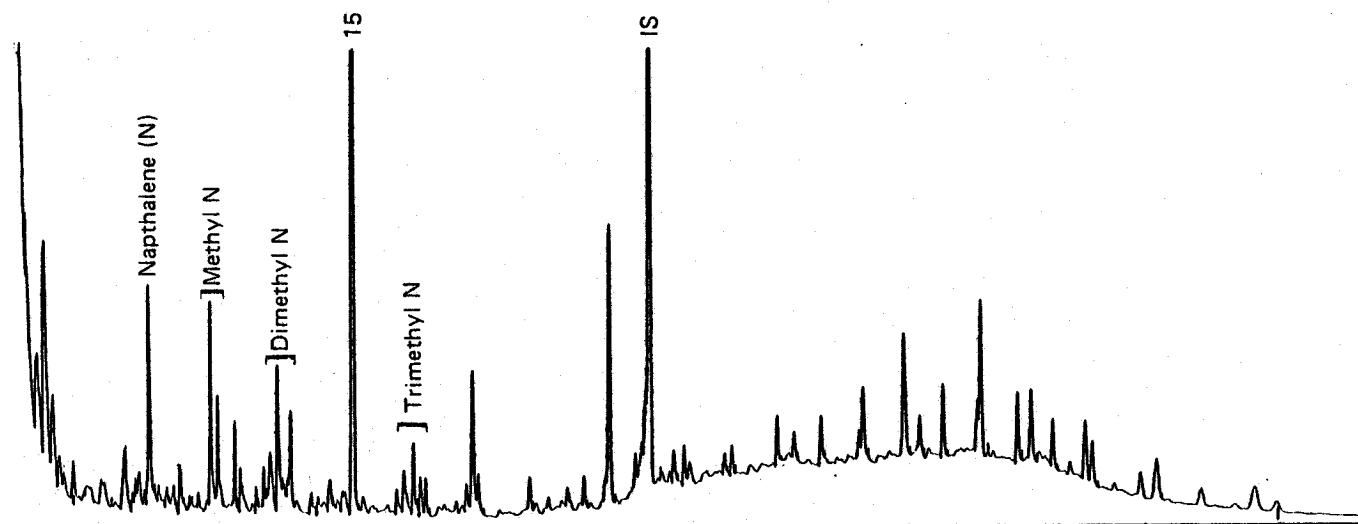


Figure 8. Gas chromatogram of seawater hydrocarbons-Class B/A.

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**Figure 9. Gas chromatogram of seawater hydrocarbons-Class A.**

Seawater Hydrocarbons  
Spring Cruise (04)  
Station B14—Weeks Island

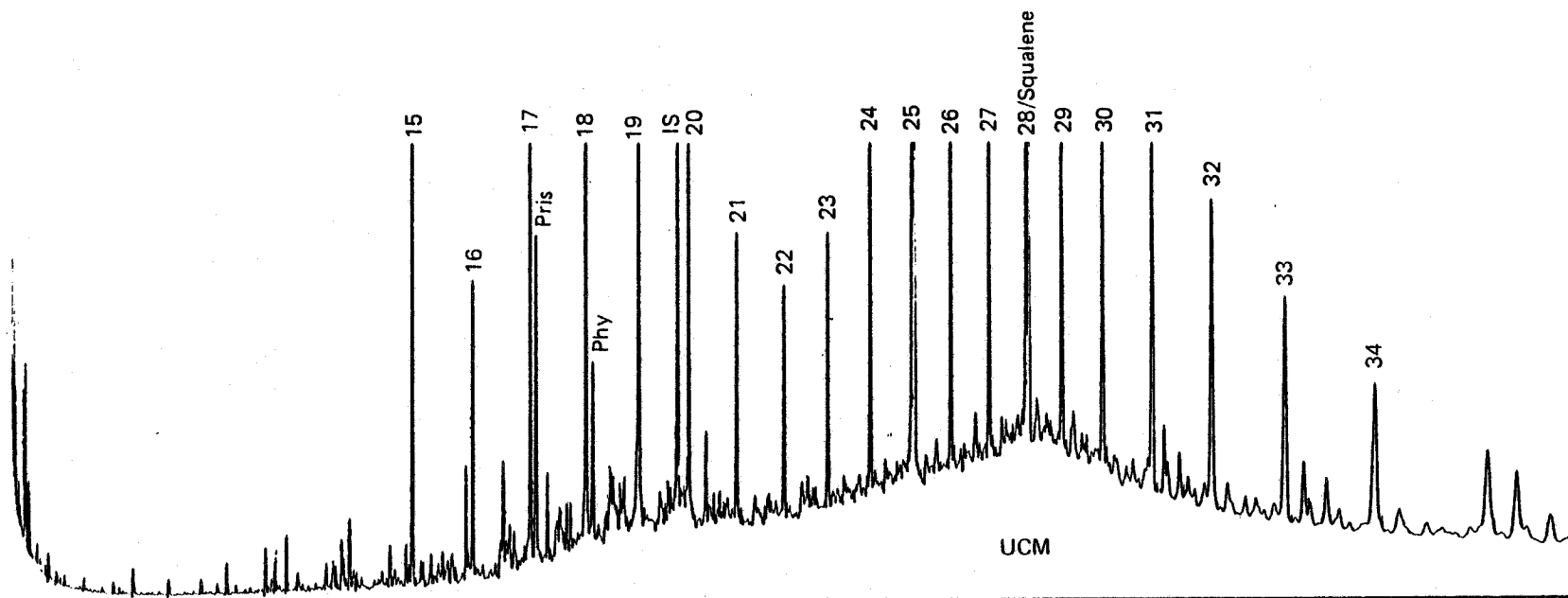


Figure 10. Gas chromatogram of seawater hydrocarbons-Class HP.

Seawater Hydrocarbons  
Winter Cruise (03)  
Station A14—West Hackberry

53

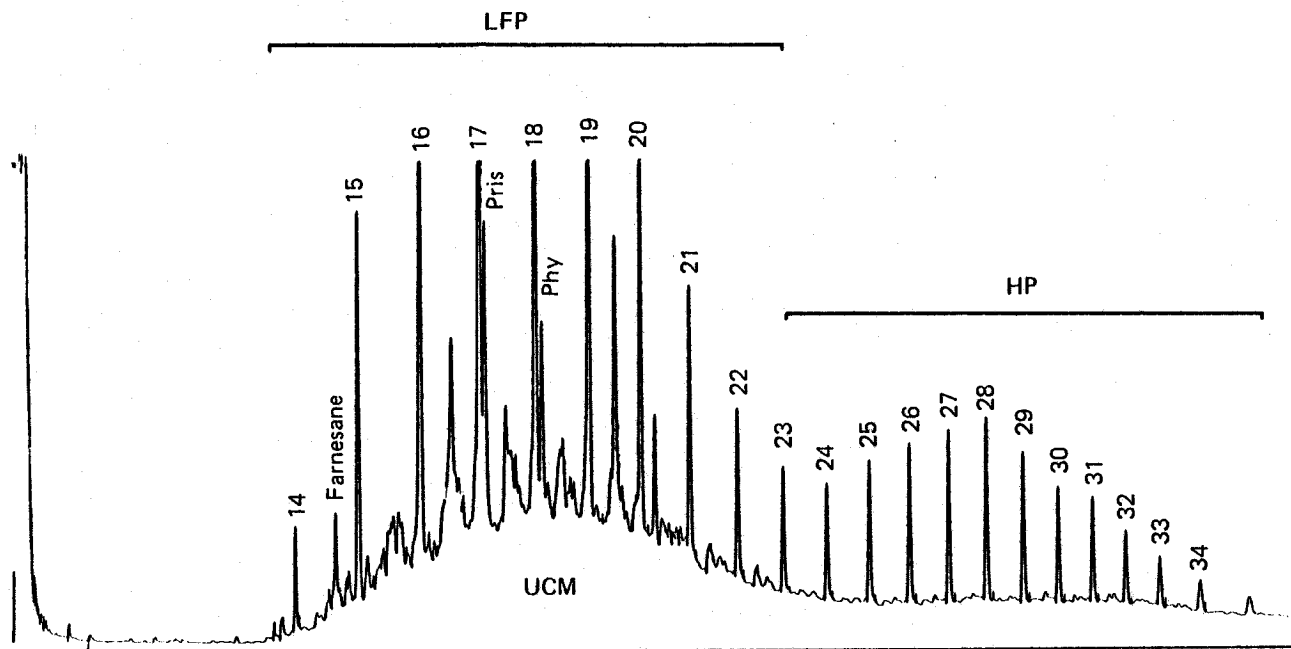


Figure 11. Gas chromatogram of seawater hydrocarbons-Class LFP/HP.

TABLE 6

SOURCE CLASSIFICATION OF SEAWATER HYDROCARBONS

SITE	STATION	SUMMER 78	FALL 78	WINTER 79	SPRING 79
West Hackberry	A2	B	B/2A	HP	B
	A5	B/2A	B-B-B <sup>a</sup>	HP	B
	A8	B/2A	B	HP	B
	A11	B/U	LFP	HP	B
	A14	2A/B	HP	LFP/HP	HP/B
Weeks Island	B2	B/2A	HP/B	HP/B	B
	B5	B/2A	B-B-B <sup>a</sup>	HP/B	HP/2A
	B8	B/2A	B/2A	B/2A	B
	B11	B	B	HP	HP/2A
	B14	B	B	HP	HP

<sup>a</sup>Denotes results of three replicates taken at these stations.

(Figure 8). The gas chromatograms of samples obtained during the first two sampling seasons indicated that the observed concentrations at both sites were due mainly to biogenic hydrocarbons with minor occasional petroleum-related inputs. No source differences were discernible that could be ascribed to geographical causes (i.e., location vis-a-vis petroleum operations, riverine runoff, etc.).

Significant changes in source materials were observed during the winter cruise. Many of the samples exhibited clear indications of petrogenic inputs which appeared to be related to high molecular weight paraffinic tar inputs characterized by a series of n-alkanes from  $C_{21}$  through  $C_{35}$  (class HP, Figure 10). This source material is apparent at both sites and is present at fairly similar concentrations on the average. However, there is much variability at the Weeks Island site. A further interpretive complication is caused by the appearance of low molecular weight shipboard (sampling) contamination in several of the Weeks Island samples (Figures 11 and 12). This is presumably related to a fuel leak observed once on-site at Weeks Island. In spite of the occurrence of this contamination at Stations 2 and 5 at Weeks Island, its presence does not seem to make a large quantitative contribution to the total hydrocarbon concentration. The high molecular weight petroleum distribution (HP) is largely attributable to weathered petroleum presumably existing in the form of small waxy tar specks (Wade and Quinn, 1975) which influenced the entire region in the winter of 1979.

At the stations where replicate samplings were conducted, a consistent trio of samples was obtained, each one largely dominated by biogenic inputs.



## Fuel Oil Contamination

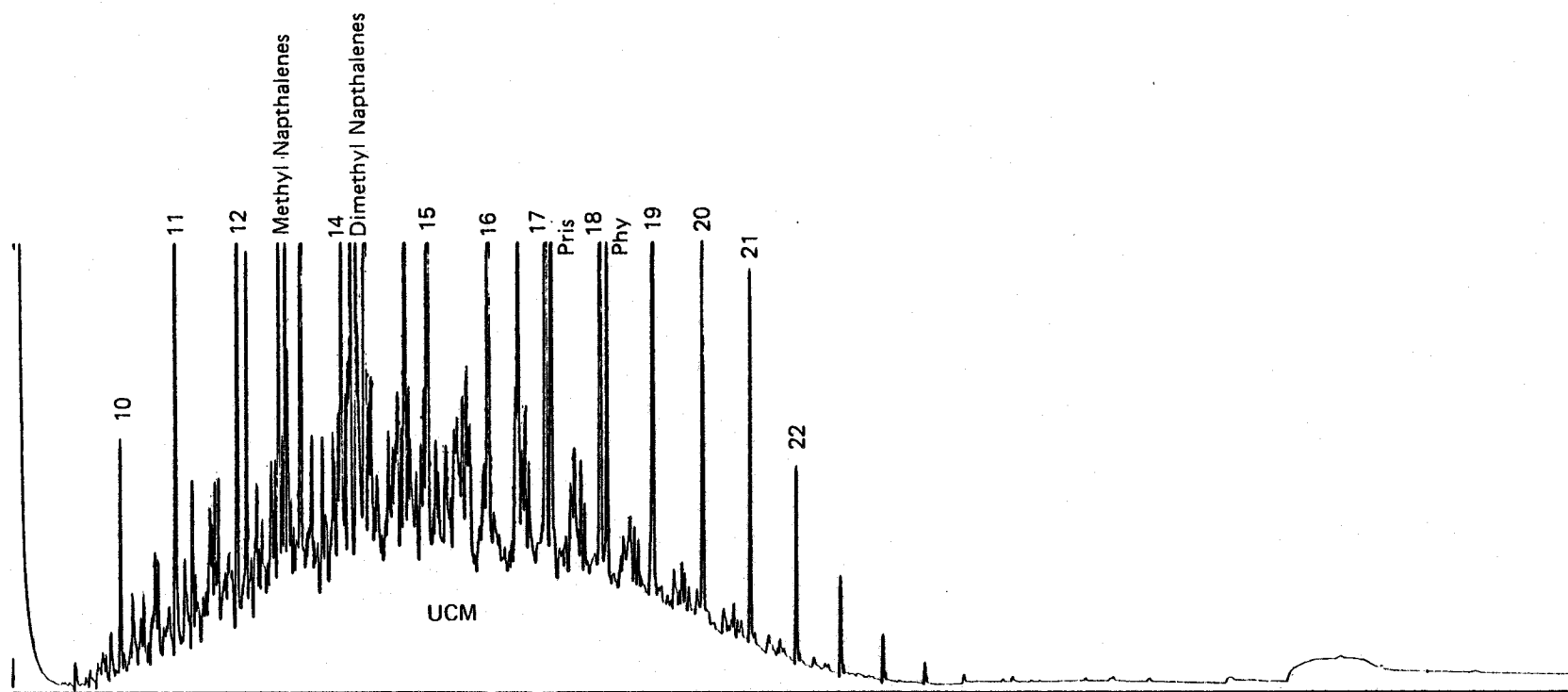


Figure 12. Gas chromatogram of ship's fuel oil.

Key individual hydrocarbon components were quantified in each water sample to evaluate any trends in the concentrations of these components and ratios of one component to another, so as to discern whether any of these compounds could be useful to a monitoring effect. The tabulations (see Appendix A) of these compounds:

1300 =  $n-C_{13}$ , a biogenic n-alkane

1500 =  $n-C_{15}$ , a biogenic n-alkane (phytoplankton)

1708 = pristane, a biogenic isoprenoid (zooplankton) or a petroleum hydrocarbon

2028 = a biogenic olefin (phytoplankton)

2800 = a biogenic polyolefin (squalene)

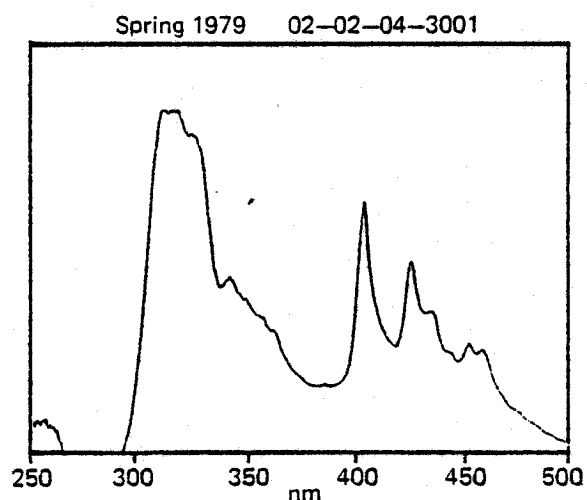
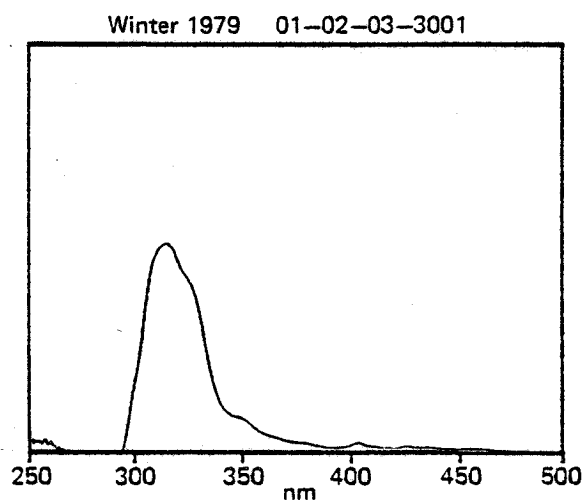
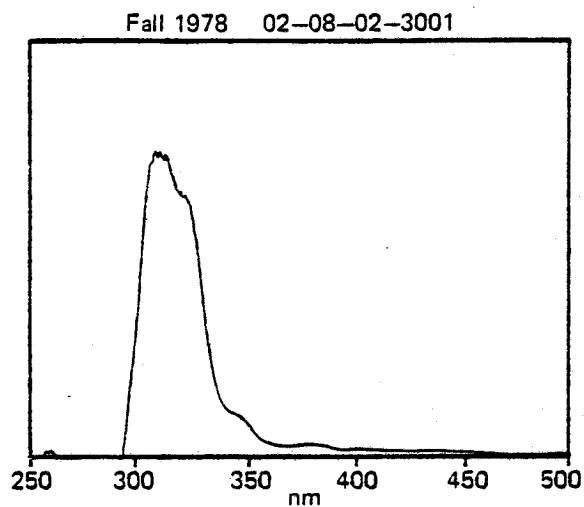
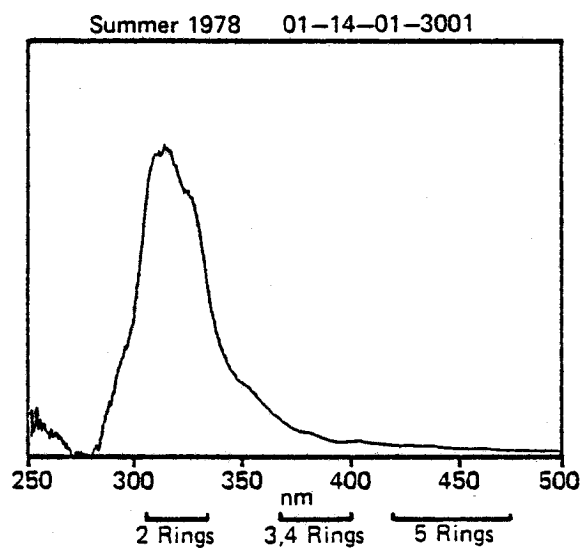
2900 =  $n-C_{29}$ , a biogenic n-alkane (terrigenous plant wax)

1708/1700 = carbon preference index, the ratio of odd to even n-alkanes in the range  $n-C_{26}$  to  $n-C_{31}$ ;  $\geq 1$  signifies a petrogenic input,  $\approx 2-5$  signifies terrigenous runoff consisting of higher plant waxes

indicate a wide variability in their concentrations both temporally and spatially.

### 3.1.2.2 Seawater Samples - Spectrofluorometry

The synchronous fluorescence spectra of the unfiltered seawater samples are consistently dominated by a narrow peak at a wavelength maximum of 310 nm (Figure 13). The peak falls within the range of 310 nm to 330 nm which corresponds to the fluorescence region for two-ringed aromatics (Lloyd, 1971). The predominance of two-ringed aromatic hydrocarbons in the seawater samples is consistent with observations made by other investigators (Gordon and Keizer, 1974; Keizer, Gordon, and Dale, 1977).



Analytical Conditions:

Synchronous Scan: 250-500 nm a 50 nm/min    Excitation Offset: -25 nm    Mode: A-B (Hexane)  
Farrand Mark I Instrument with Corrected Excitation and Emission.

Figure 13. Typical fluorescence spectra of seawater samples (see text for explanation).

The predominance of two-ringed aromatics in the unfiltered seawater samples could be the result of either the abundance of two-ringed aromatics in the hydrocarbon source material or selective solubilization of two-ring aromatics from a source material containing two- to five-ringed aromatics. Common hydrocarbon sources enriched in two-ring aromatics are No. 2 fuel oil and diesel oil. Leakages and spillages from ships and boats operating in the nearshore regions no doubt contribute two-ring aromatics to the water column.

Selective solubilization of two-ring aromatics results from their high solubility relative to aromatic hydrocarbons with a greater number of rings (Zurcher and Thuer, 1978; Winters & Parker, 1978). Seawater that contacts a crude oil which contains a variety of aromatic ring structures will become highly enriched in two-ring aromatic hydrocarbons. Only relatively small amounts of higher molecular weight aromatics will be dissolved. Given the large number of producing offshore oil wells and the proximity of the two sites to terrestrial runoff, selective solubilization is a likely source for the hydrocarbons of the water column.

With the exception of certain samples collected during the winter and spring, 1979 samplings, no aromatics other than two-ring aromatics are present in the samples. This suggests that the suspended particulates in the water do not contribute substantial amounts of aromatics to the samples since particulates preferentially absorb the less soluble higher molecular weight aromatics (Meyers and Quinn, 1973; Zurcher and Thuer, 1978).

However, a number of the samples collected in January and May, 1979 have a characteristic set of fluorescence peaks in the 350 nm to 450 nm region of their spectra (Figure 14). The same set of peaks occurs in the spectra of an intercalibration sediment sample (NOAA, OCSEAP program) containing primarily polynuclear aromatic hydrocarbons (PAH's) from a pyrolytic source, e.g., forest fires or fossil fuel combustion (Figure 14). The PAH's in these samples could be derived from either the diesel exhaust from the sampling platform or terrestrial runoff with high concentration of PAH's derived from fossil fuel combustion such as from power plant exhaust or the West Hackberry fire.

Quantitatively, the spectrofluorometry data show no significant interstation differences at a given site. Since tidal and wind-driven movement of the water over a day far exceeds the distance between stations, no consistent interstation trends in the concentrations of aromatics dissolved in the water column data are expected. However, it should be noted that if the suspended particulates had contributed significant amounts of aromatic hydrocarbons present in the seawater sample, trends relating hydrocarbon concentration to water depth might be anticipated.

The seasonal average concentration of fluorescence-derived hydrocarbons (FD hydrocarbons) in water samples collected in the vicinity of the West Hackberry and Weeks Island sites ranged from 0.8 to 4.0  $\mu\text{g/l}$  (Table 7). These values are similar to fluorescence-derived (FD) values found in other coastal regions (Keizer, Gordon and Dale, 1974).

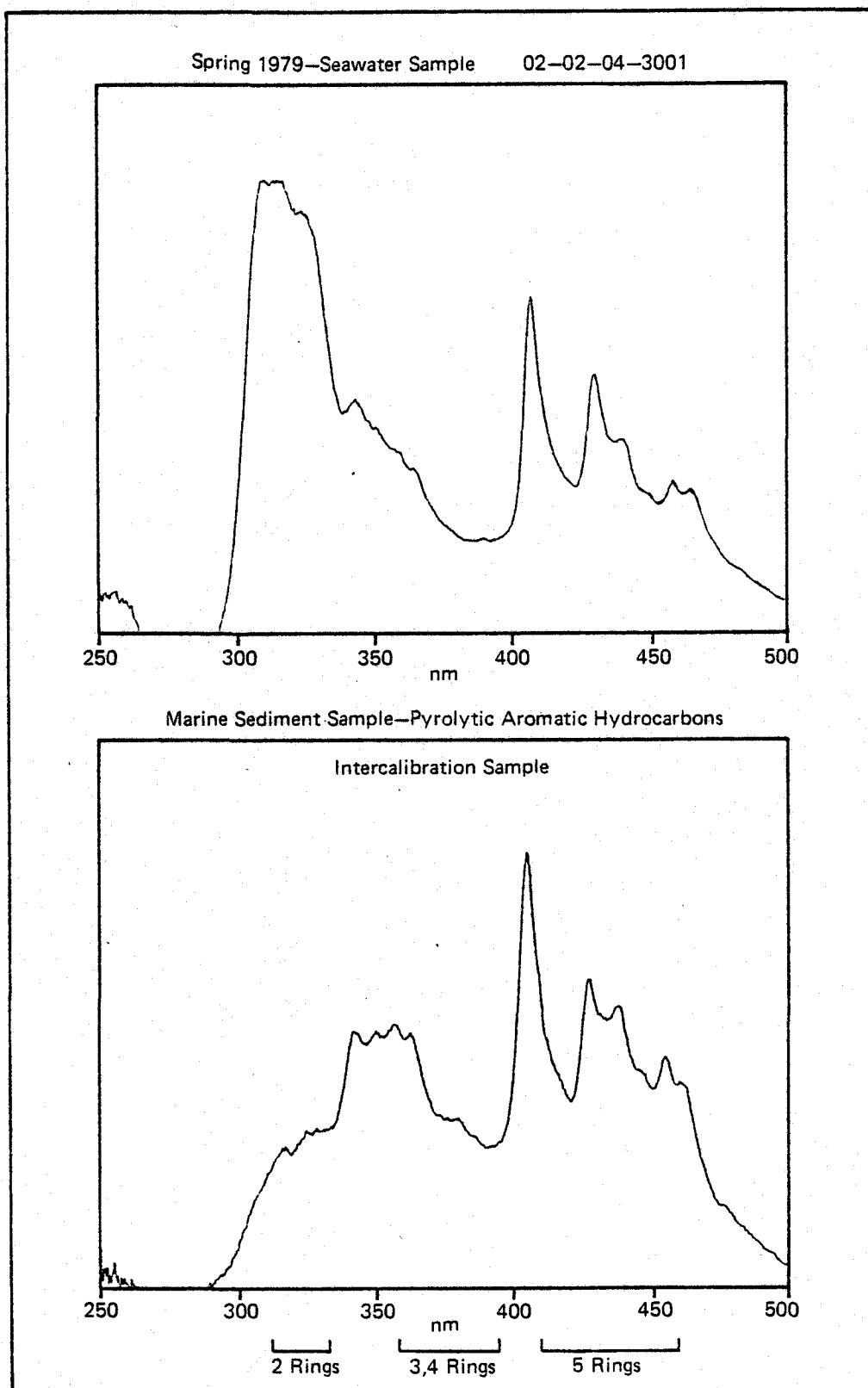


Figure 14. A comparison of the fluorescence spectra of a seawater sample with a marine sediment which contains polynuclear aromatic hydrocarbons from a pyrolytic source.

TABLE 7

WATER COLUMN SPECTROFLUOROMETRIC DATA  
( $\mu\text{g/l}$  equivalents)<sup>a</sup>

SEASON	WEST HACKBERRY			WEEK ISLAND		
	312 nm	328 nm	348 nm	312 nm	328 nm	348 nm
Summer 1978	2.8 $\pm$ 1.9	3.5 $\pm$ 2.3	0.0	1.9 $\pm$ 1.1	1.8 $\pm$ 1.1	0.0
Fall 1978	1.9 $\pm$ 0.4	1.9 $\pm$ 0.5	0.0	0.8 $\pm$ 0.4	0.7 $\pm$ 0.3	0.0
Winter 1979	4.0 $\pm$ 1.2	3.0 $\pm$ 1.4	0.8 $\pm$ 0.4	1.7 $\pm$ 0.5	1.0 $\pm$ 0.3	0.3 $\pm$ 0.2
Spring 1979	2.5 $\pm$ 0.9	2.0 $\pm$ 0.8	0.8 $\pm$ 0.8	2.5 $\pm$ 2.0	2.1 $\pm$ 1.6	0.8 $\pm$ 0.7
REPLICATE DATA (OCTOBER 1978 SAMPLING)						
	312 nm		328 nm			
Station 5A	2.4 $\pm$ 0.9		2.6 $\pm$ 0.9			
Station 5B	0.7 $\pm$ 0.2		0.6 $\pm$ 0.2			

<sup>a</sup>Concentrations expressed in  $\mu\text{g/g}$  of No. 2 fuel oil (API Reference No. 2).

No significant seasonal trends are evident. However, the mean concentrations of FD hydrocarbons at the West Hackberry Site are, with the exception of the spring 1979 sampling, significantly higher than concentrations at the Weeks Island site.

### 3.2 Surface Sediments

The surface sediment samples obtained and analyzed for their hydrocarbon content and composition were pooled samples of four replicate grabs. In the fall, both the pooled sample and the individual replicates were analyzed to establish (1) the adequacy of the pooling method and (2) the small-scale spatial distribution of hydrocarbons (i.e. patchiness). Surface sediment represents a sink for waterborne pollutants and a semipermanent record of environmental exposure to pollutants such as hydrocarbons (NAS, 1975). As the habitat for many important epifauna and infauna which are commercially important or ecologically important as food for commercial species, the sediment analysis is a key in environmental baseline and monitoring studies.

#### 3.2.1 Hydrocarbon Concentrations

Total concentrations of hydrocarbon compounds in surface sediment from the two sites are summarized graphically in Figures 15 and 16, and tabulated for each station, Table 8, and for each site seasonally, Table 9. Detailed compositional information is tabulated in Tables in the Appendix. The data reveal that:



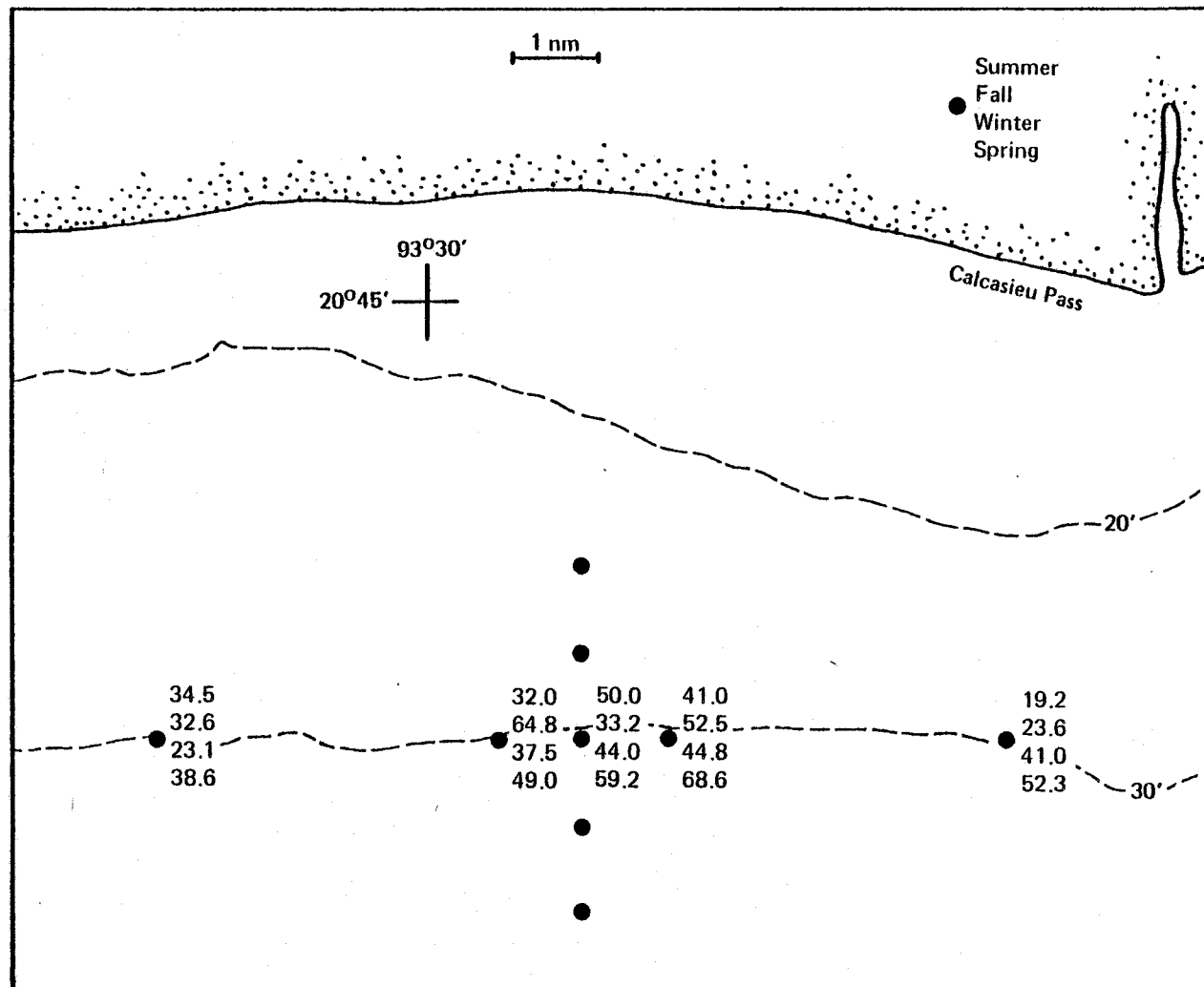


Figure 15. Surface Sediment Hydrocarbon Concentrations, West Hackberry ( $\mu\text{g/g} = \text{ppm}$ ).

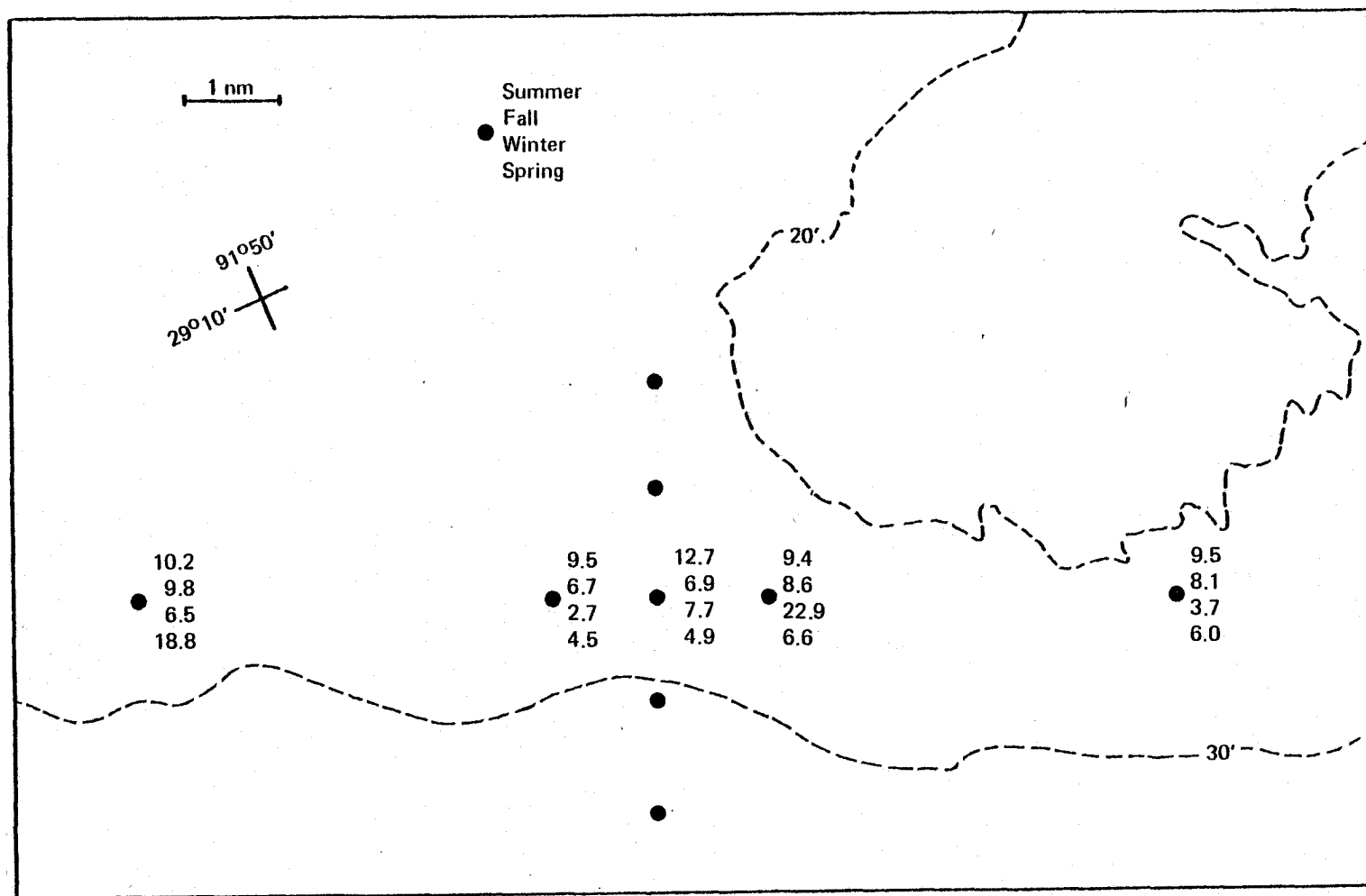


Figure 16. Surface Sediment Hydrocarbon Concentrations, Weeks Island ( $\mu\text{g/g} = \text{ppm}$ ).

TABLE 8

SURFACE SEDIMENT HYDROCARBON  
CONCENTRATIONS<sup>a</sup> BY STATION

<u>Site</u>	<u>Station</u>	<u>Concentration - All Seasons</u>	<u><math>\sigma/\bar{x}</math></u>
West Hackberry	A2	32.2±6.6	.20
	A5	45.8±14.5	.32
	A8	46.6±10.9	.23
	A11	51.7±12.2	.24
	A14	34.0±15.4	.45
Weeks Island	B2	11.3±5.3	.47
	B5	5.9±2.9	.49
	B8	8.1±3.3	.41
	B11	11.9±7.4	.62
	B14	6.8±2.5	.38

<sup>a</sup>  $\mu\text{g/g} = \text{ppm}$

TABLE 9

SURFACE SEDIMENT HYDROCARBON CONCENTRATIONS<sup>a</sup> BY SITE

SITE		SUMMER	FALL	WINTER	SPRING	TOTAL
West	Concentr.	35.3+11.4	41.3+16.8	38.1+8.9	53.5+11.2	42.1+13.4
Hackberry	( $\sigma/\bar{x}$ )	(.32)	(.41)	(.23)	(.21)	(.32)
Weeks	Concentr.	10.3+1.4	8.0+1.3	8.7+8.2	8.2+6.0	8.8+4.8
Island	( $\sigma/\bar{x}$ )	(.14)	(.16)	(.94)	(.73)	(.55)

<sup>a</sup> $\mu\text{g/g} = \text{ppm}$

1. The sediment chemistry differs markedly between the two sites. The siltier sediments at West Hackberry contain 3.5 to 6.5 (average 4.8) times as much hydrocarbon material as do the sandier Weeks Island sediments.
2. Small variations in concentration do occur within each site (Table 9) but are far less than the between-site variations.
3. The variability within each site for the entire year ( $\underline{s}/\bar{x} = .32$  at West Hackberry and 0.55 at Weeks Island) is equivalent to the average within-station variability ( $\underline{s}/\bar{x} = 0.29$  at West Hackberry and 0.48 at Weeks Island) at each site. In other words, over a year each site appears to be adequately defined by the average of the individual stations.
4. Gravimetrically determined hydrocarbon levels (Figures 15 and 16; Tables 8 and 9) are in excellent agreement with those determined by gas chromatography alone (i.e., sum of GC peaks plus unresolved complex mixture - (hump); see Tables in Appendix.

A pooling experiment was performed on samples collected during the fall 1978 cruise. The results for the total hydrocarbon levels are presented in Table 10. Three important pieces of information are revealed by this experiment:

TABLE 10

SEDIMENT POOLING EXPERIMENT  
FALL CRUISE

Site	Station	Total Hydrocarbon Pooled	Concentrations $\bar{x}(1-4)$	$\sigma/\bar{x}$
West Hackberry	A2	32.6	35.5 $\pm$ 8.9	.25
	A8	33.2	48.7 $\pm$ 13.5	.28
	A14	23.6	39.3 $\pm$ .4	.31
Weeks Island	B2	9.8	11.3 $\pm$ 5.4	.48
	B8	6.9	10.1 $\pm$ 2.3	.23
	B14	8.1	6.3 $\pm$ 2.6	.42

1. The within-station variability (replicate grabs of sediment) is 25-31 percent at the West Hackberry site and 23-48 percent at the Weeks Island site. This variability is consistent with similar within-station variabilities reported for different geographical areas (e.g., Boehm and Quinn, 1978).
2. Percent variability increases with decreasing absolute hydrocarbon levels.
3. The within-station variability is roughly equivalent to the within-site variability (see Table 9).
4. The average of the individual replicates appears to be somewhat higher than the pooled sample concentration. However, in all cases the pooled value is equivalent to the mean of the replicates at the 95 percent confidence level.

Hydrocarbon concentrations at West Hackberry determined in this study are consistently 3-4 times higher than those previously reported (DOE, 1978). The cause for this discrepancy is not known and, although different stations were sampled during different seasons, the discrepancy is greater than accountable for by small scale spatial or temporal variation.

### 3.2.2 Hydrocarbon Composition

#### 3.2.2.1 Gas Chromatography

The examination of gas chromatograms of hydrocarbons in surface sediments from the two sites reveals, for the most part, a uniform basic composition consisting of:

1. A large unresolved complex mixture (UCM) of coeluting hydrocarbons, presumably of naphthenic and naphtheno-aromatic structure (cyclic), probably indicative of weathered pollution inputs.
2. Resolved hydrocarbons, the most frequently observed of which are pristane,  $n\text{-C}_{15}$ ,  $n\text{-C}_{18}$ , a series of cycloolefins eluting between retention indices of 2040 to 2120, odd chain  $n$ -alkanes from  $n\text{-C}_{23}$  to  $n\text{-C}_{31}$ ; polycyclic aliphatic compounds (pentacyclic triterpanes = hopanes) eluting from  $n\text{-C}_{27}$  to  $n\text{-C}_{31}$  and squalene (a polyolefin eluting just after or with  $n\text{-C}_{28}$ ).

Figures 17 through 20, representing gas chromatograms from both sites, illustrate these compositional features. These main features indicate that the hydrocarbon composition of all sediment samples examined consists of degraded anthropogenic inputs (UCM), terrigenous plant material ( $n\text{-C}_{23}$  to  $n\text{-C}_{31}$  odd numbered alkanes), biosynthesized hydrocarbons, and indications of degraded petroleum (hopanes). The presence of the pentacyclic triterpanes (hopanes) do not alone signify petroleum. However, as Dastillung and Albrecht (1976) discuss, the hopanes having greater than 30 carbons are present in near 1:1 ratios of the two diastereomers, thus indicating a petrogenic input. (This was confirmed by GC/MS searches for  $m/e = 191$  and quantifying the diastereomers).



Surface Sediment Hydrocarbons  
Fall Cruise (02)  
Station A14—West Hackberry

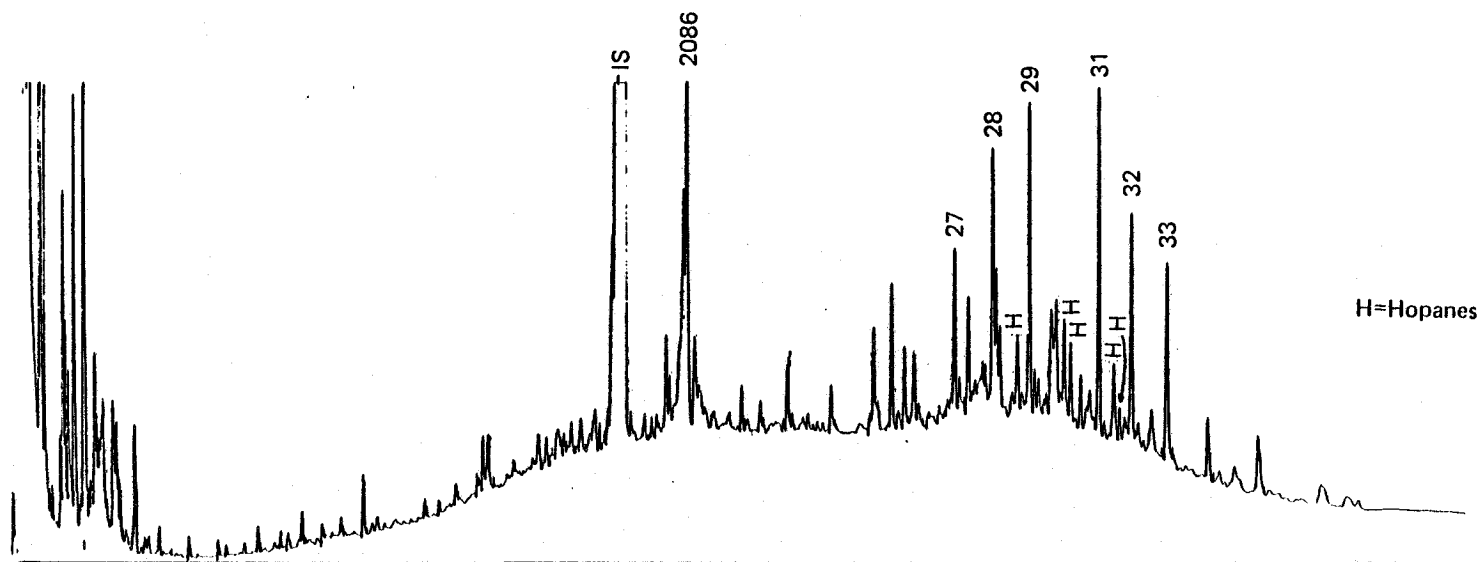


Figure 17. Gas chromatogram of surface sediment.

Surface Sediment Hydrocarbons  
Spring Cruise (04)  
Station B2—Weeks Island

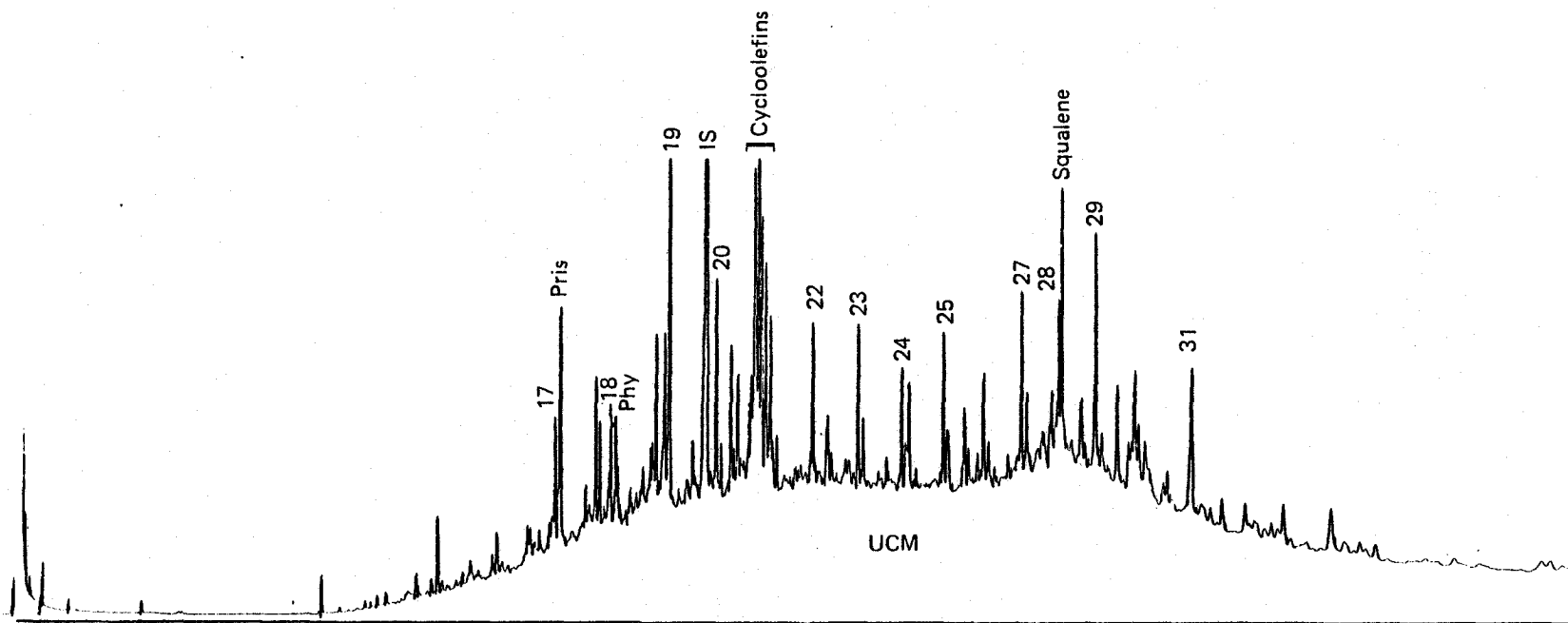


Figure 18. Gas chromatogram of typical surface sediment-Weeks Island.

Surface Sediment Hydrocarbons  
Spring Cruise (04)  
Station A2—West Hackberry

95

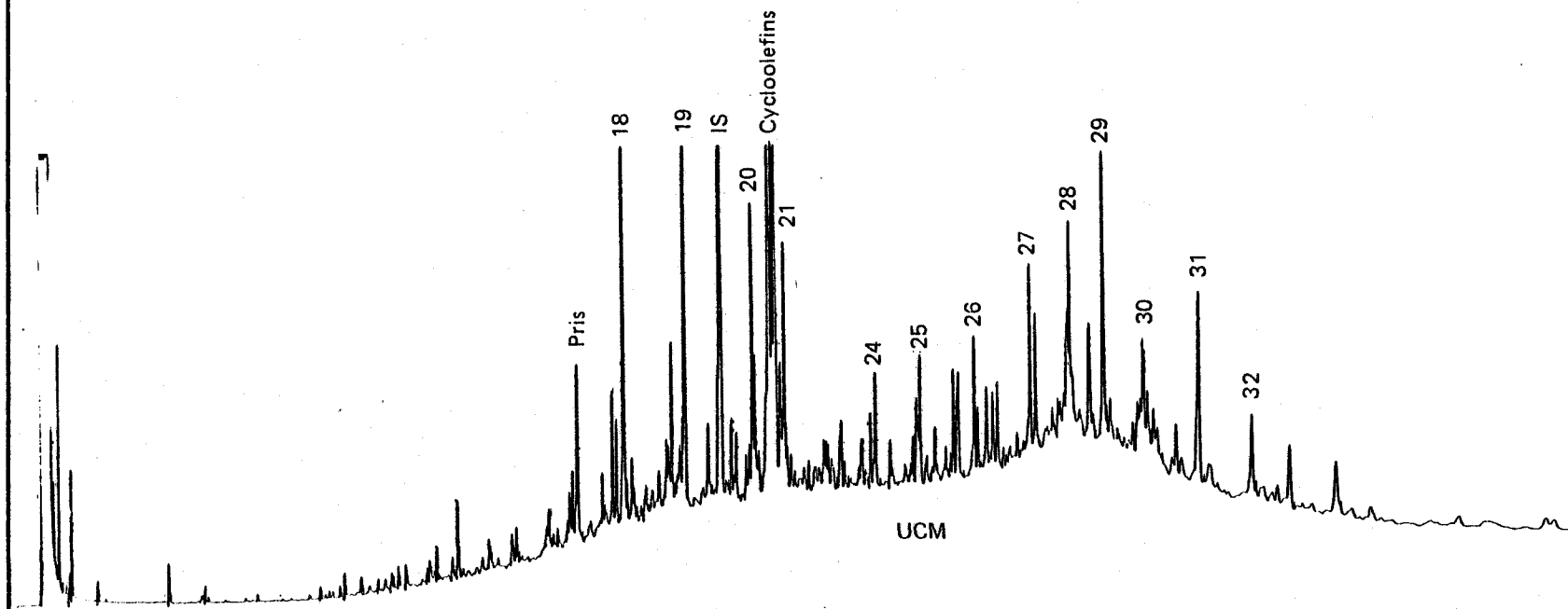


Figure 19. Gas chromatogram of surface sediment hydrocarbons.

Surface Sediment Hydrocarbons  
Winter Cruise (02)  
Station A2—West Hackberry

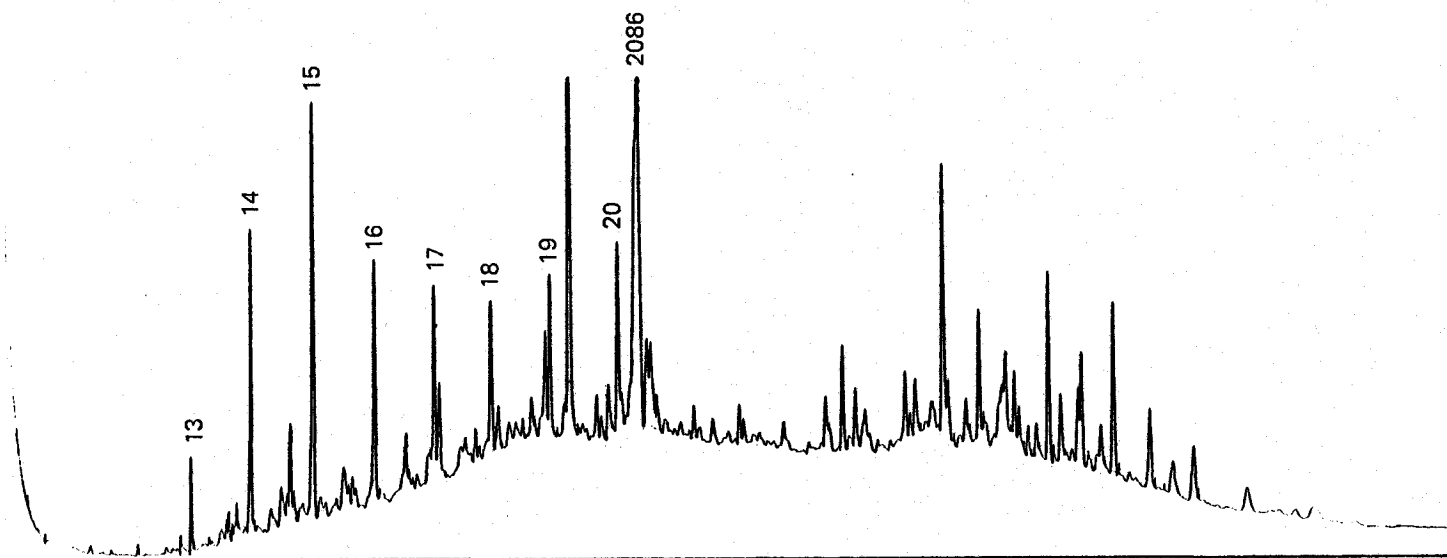


Figure 20. Gas chromatogram of surface sediment hydrocarbons showing low molecular weight distributions.

No fresh or recent petroleum inputs are seen in the gas chromatograms. This is evidenced by the absence of a homologous series of n-alkane peaks which are predominant in almost all crude oils and which are degraded on a time scale of months following an oil spill. The source materials as revealed by the GC traces are nearly identical at all stations from both sites. Concentrations of these compounds are a function of sediment texture and total organic carbon levels (see section 3.2.4) and are dictated by physical forcing factors affecting deposition and sediment transport in the region. The area-wide hydrocarbon composition in the sediment appears to be quite uniform, varying neither temporally nor spatially.

As discussed by Reed et al. (1977), compositional features attributable to petroleum include:

1. an extended homologous series of normal alkanes, exhibiting an odd-to-even ratio of approximately unity
2. an homologous series of isoprenoid alkanes ( $C_{15}$ - $C_{21}$ ), where the ratios between adjacent pairs are approximately unity (except for ratios including the  $C_{17}$  isoprenoid, which is invariably present in low concentrations)
3. multiple homologous series of saturated cycloalkanes (i.e., steranes and triterpanes)
4. multiple homologous series of alkyl substituted benzenes and polycyclic aromatic hydrocarbons
5. an unresolved envelope (UCM) may be a characteristic of weathered petroleum.

The composition of sediments in the West Hackberry and Weeks Island sites illustrates items 3, 4 and 5 to varying extents and is typical of many offshore fine-grained sediments exhibiting a composite distribution of weathered petroleum-related material and marine and terrigenous biogenic inputs. However, several samples which exhibited the n-C<sub>13</sub> to n-C<sub>19</sub> smooth n-alkane distribution shown in Figure 20 may have been influenced by small amounts of a recent petroleum input.

Aromatic hydrocarbon distributions are revealed by a limited use of GC/MS (Section 3.2.2) and the extensive use of UV-spectrofluorometry (Section 3.2.3).

#### 3.2.2.2 Hydrocarbon Composition - Gas Chromatographic Mass Spectrometry (GC/MS)

During this study, several samples were analyzed in detail by glass capillary GC/MS. These analyses revealed levels of polycyclic aromatic hydrocarbons (PAH) and the nature of the polycyclic aliphatic distributions (hopanes). These details are not discernible by GC alone due to the relatively low levels of these compounds in the entire chromatogram. Seasonal GC/MS runs were performed at station A2, West Hackberry, to examine any seasonal trends in PAH composition and concentrations and to determine the source of these PAH compounds. These quantitative data are presented in Table 11.

Several homologous series of alkyl substituted polycyclic aromatic hydrocarbons and organo-sulfur (dibenzothiophenes) compounds are revealed. Concentrations of the following types of aromatic compounds are:

TABLE 11

PAH CONCENTRATIONS<sup>a</sup> IN SURFACE  
SEDIMENT REVEALED BY GC/MS

	M/C	CRUISE 01	CRUISE 02	CRUISE 03	CRUISE 04
Naphthalene	129	214	9	33	30
C1 "	142	87	22	21	36
C2 "	156	87	59	39	52
C3 "	170	-	75	31	38
C4 "	184	-	43	17	9
Biphenyl	154	-	8	1	8
Fluorene	166	-	4	5	16
C1 "	180	-	7	3	24
C2 "	194	-	13	16	41
C3 "	208	-	5	24	58
Phenanthrene	178	119	41	32	64
C1 "	192	151	48	42	124
C2 "	206	133	48	47	104
C3 "	220	65	32	34	74
C4 "	234	-	16	6	-
Dibenzothiophene	184	-	15	7	-
C1 "	198	-	20	12	8
C2 "	212	21	27	20	21
C3 "	226	-	17	14	8
Fluoranthene	202	72	39	36	81
Pyrene	202	100	48	42	90
Benzo(a)anthracene	228	86	39	31	19
Chrysene	228	-	-	-	38
Benzofluoranthenes	252	-	37	34	
Benzo(a) pyrene	252	-	4	12	16
Benzo(e) pyrene	252	-	14		
Perylene	252	542	147	188	321

<sup>a</sup>All concentrations in ng/g

Naphthalenes	150-222 ng/g
Fluorenes	30-130 ng/g
Phenanthrenes	160-470 ng/g
Dibenzothiophenes	20-80 ng/g
Fluoranthene/pyrene	80-170 ng/g
Benzanthracene/chrysene	30-80 ng/g
Benzopyrenes	10-20 ng/g
Perylene	180-540 ng/g

According to Laflamme and Hites (1978) and Windsor and Hites (1979), these concentration levels observed at West Hackberry are intermediate to those found in river basins surrounding industrialized areas and background levels found in continental shelf sediment. This indicates that the two study sites are indeed influenced by runoff and seaward transport of sediment from industrialized river basins. Presumably, although not confirmed by GC/MS in this study, levels of PAH compounds are less at the Weeks Island site; if one assumes that PAH levels follow total hydrocarbon levels, then PAH levels at Weeks Island are approximately one-third the West Hackberry levels. UV-spectrofluorometric analyses (see next section) do, however, confirm these precise differences between PAH levels at the two sites.

The PAH composition (partly revealed in Figure 21) indicates that the observed compound concentration levels are due to a mixture of PAH compounds due to pyrolytic inputs (i.e., the combustion of fossil fuels followed by direct offshore transport), those due to petroleum influences and those due to in situ diagenetic production. Pyrolytic input is suggested by the significant levels of parent compounds



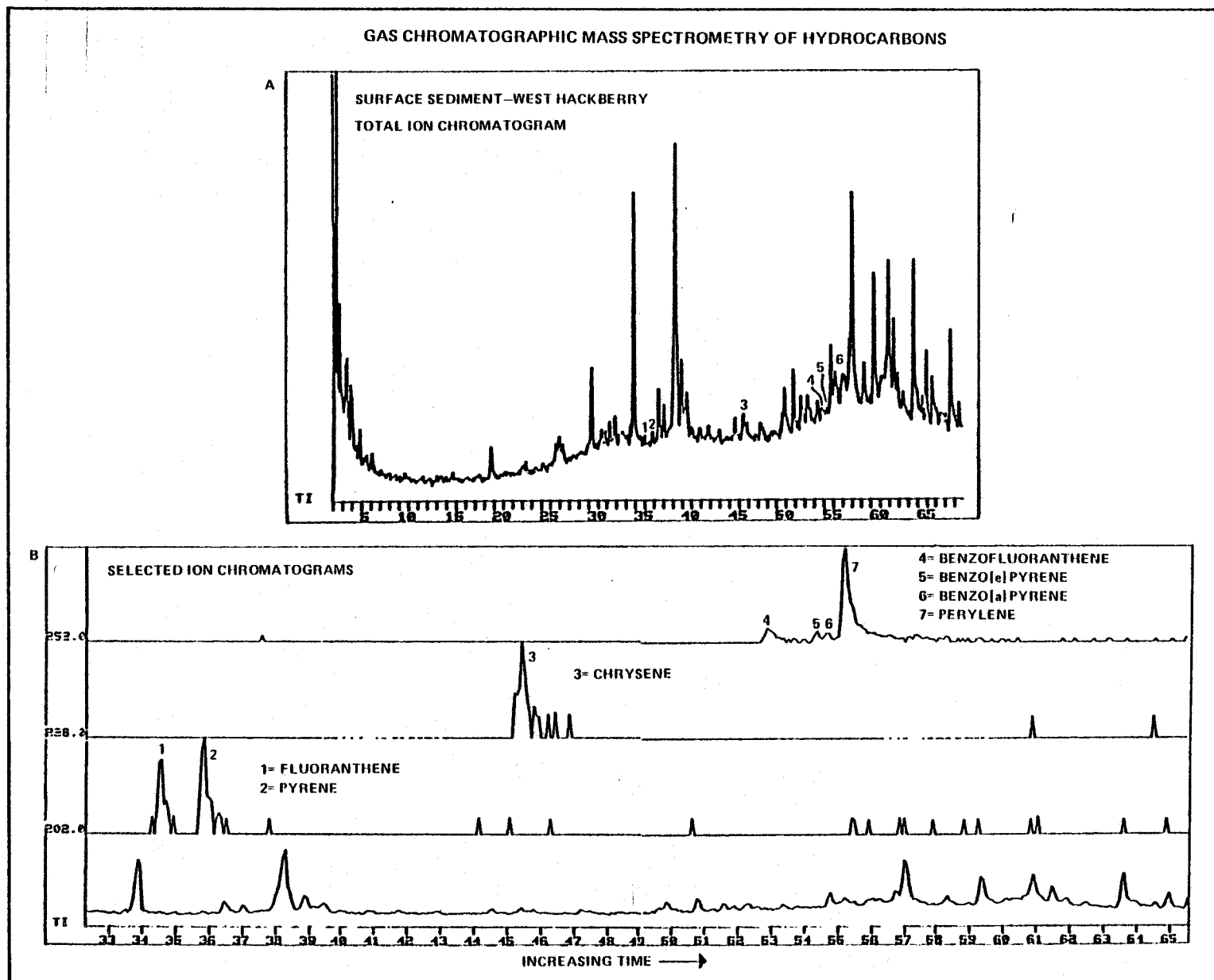


Figure 21. Mass spectral searches for selected PAH compounds in surface sediment.

phenanthrene, fluoranthene and pyrene. Petroleum influence is strongly suggested by the high levels of alkyl naphthalenes, alkyl phenanthrenes and dibenzothiophenes relative to parent (unsubstituted) compounds (Youngblood and Blumer, 1975). Diagenetic production is strongly suggested by the presence of high levels of perylene. It has been hypothesized that this five-ringed PAH is formed in sediment through the reduction of pigments. Aizenshtat (1973) hypothesized that environmental transformation of pigments into perylene requires their rapid deposition into a reducing sediment. However, we have found perylene in the oxidizing sediments of Weeks Island as well as in the reducing sediments at the West Hackberry site.

#### 3.2.2.3 Surface Sediment Samples - Spectrofluorometry

Unlike those of the seawater samples, the fluorescence spectra of surface sediment samples contain substantial quantities of two-, three-, and four- and five-ring aromatic hydrocarbons (Figures 22-24). Two features are common to all of the bottom sediment spectra: a moderately resolved peak with a maximum height at 312 nm and a pair of sharp peaks at 438 and 462 nm. Although the maximum of the 312 nm peak falls in the spectral range of two-ring aromatics (310-330 nm), a substantial portion of the peak areas lies in the three- and four-ring aromatic spectral range (340-380 nm). This portion of the bottom sediment sample spectra is similar to spectra of Bunker C and crude oils which contain two-, three-, four- and five-ring aromatic hydrocarbons (Figure 22).

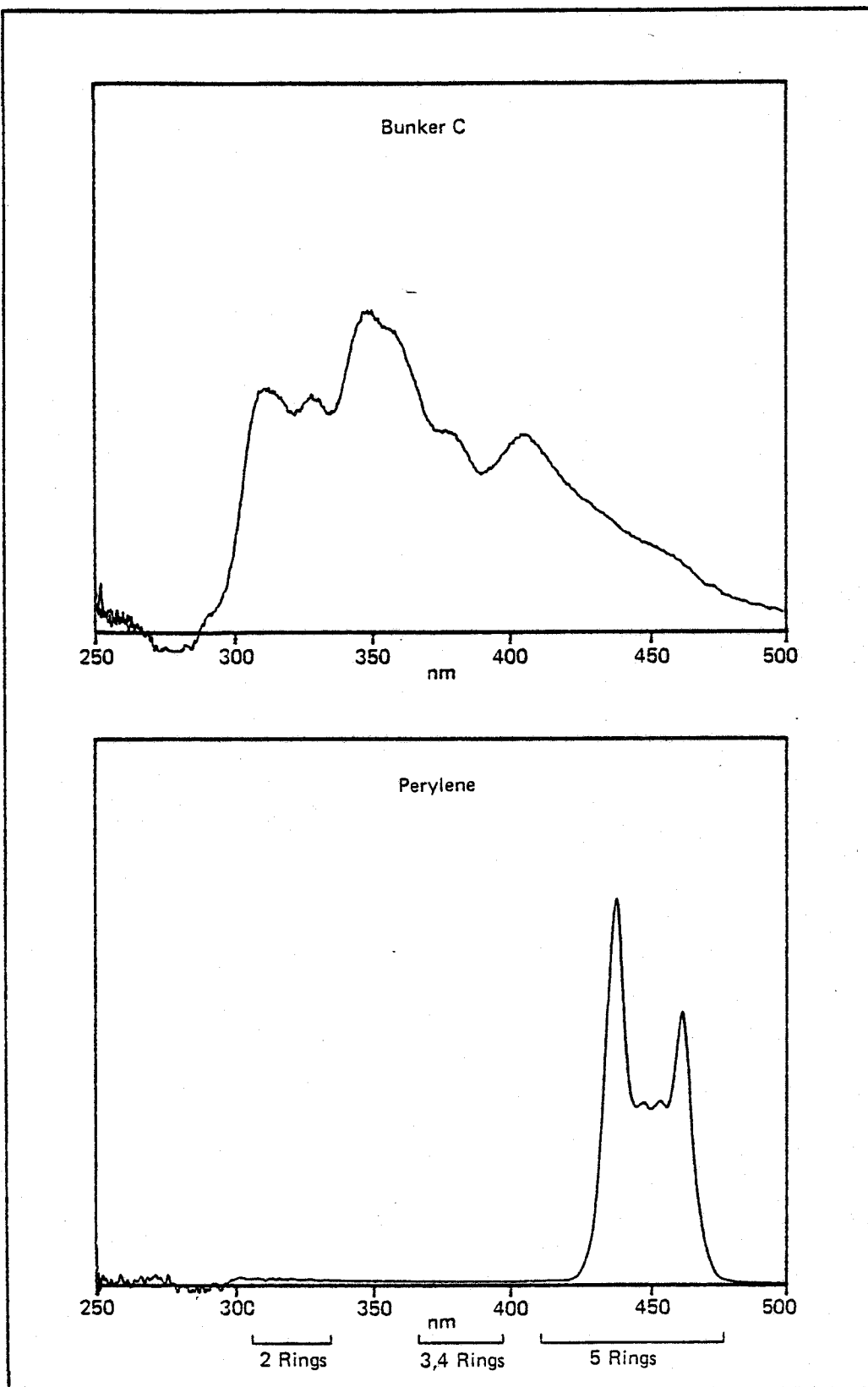
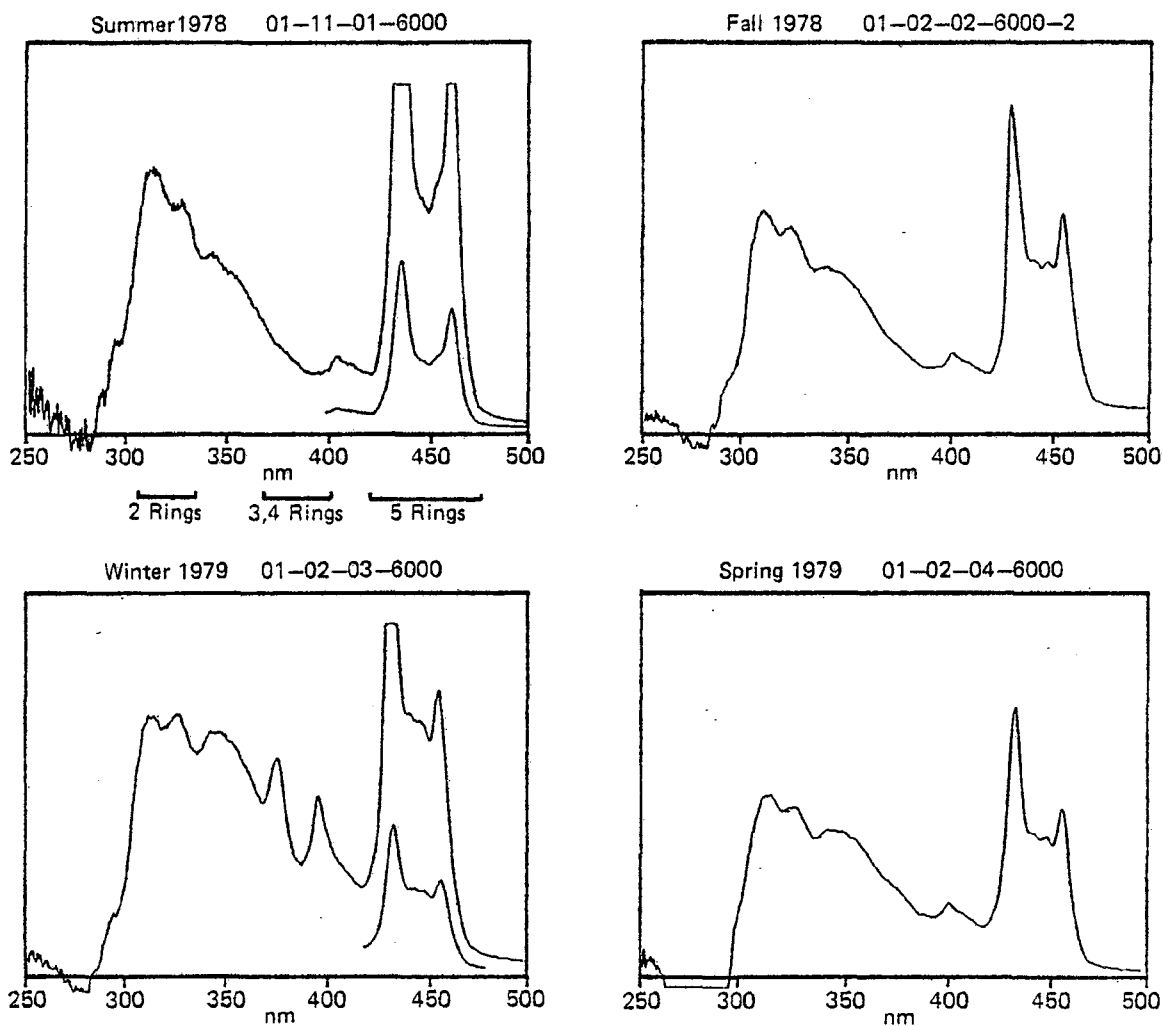
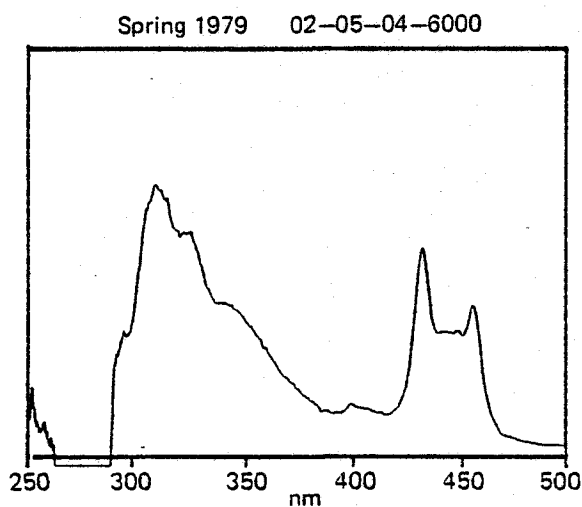
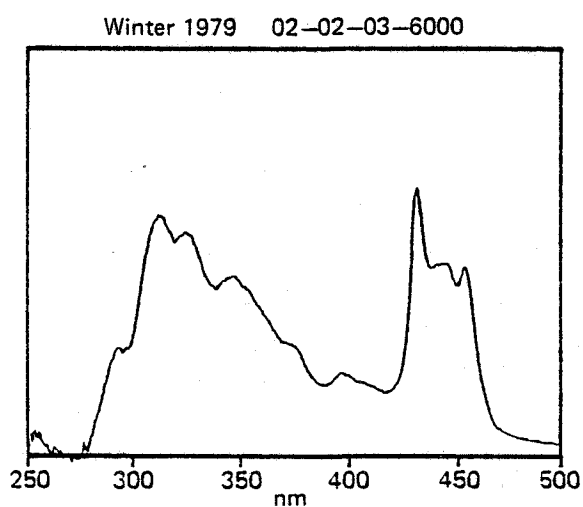
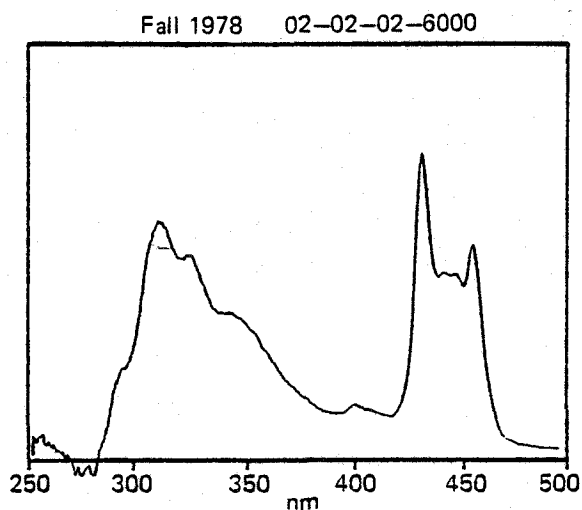
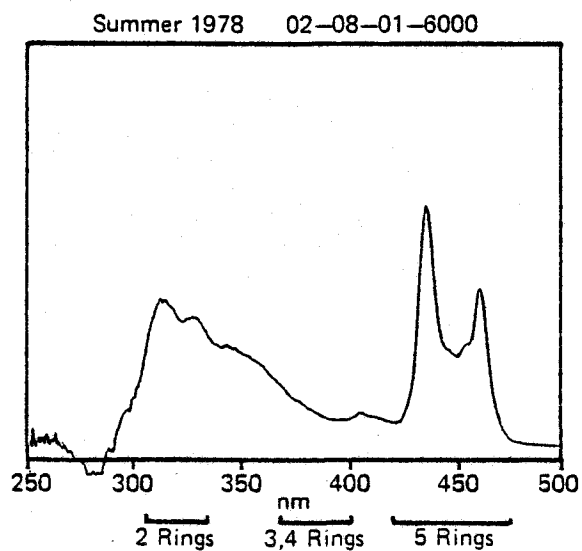


Figure 22. Fluorescence spectra of Bunker C oil and perylene.



Analytical Conditions:  
 Synchronous Scan: 250-500 nm a 50 nm/min    Excitation Offset: -25 nm    Mode: A-B (Hexane)  
 Farrand Mark I Instrument with Corrected Excitation and Emission.

Figure 23. Typical fluorescence spectra of surface sediment samples, West Hackberry Site.



Analytical Conditions:

Synchronous Scan: 250-500 nm a 50 nm/min Excitation Offset: -25 nm Mode: A-B (Hexane)  
 Farrand Mark I Instrument with Corrected Excitation and Emission.

Figure 24. Typical fluorescence spectra of surface sediment samples, Weeks Island Site.

The most likely source of the two-, three-, and four-ring aromatics to the sediments is petroleum hydrocarbons associated with terrestrial runoff, spilled during offshore drilling operations and discharged from tankers, freighters, and other ships.

The pair of peaks at 438 and 462 nm has been noted previously in fluorescence spectra of lake sediments and identified as perylene, a five-ring aromatic hydrocarbon (Wakeham, 1977). A comparison of a spectrum of perylene (Figure 22) with the spectra of bottom sediment samples confirms the correlation of the 438 nm/462 nm pair and perylene. The marked predominance of the perylene peaks in the bottom sediment spectra results from the high quantum efficiency of perylene compared to the quantum efficiency of other aromatic hydrocarbons. The concentrations of perylene are actually much lower than concentrations of other aromatic-ring groups even though visual inspection of the spectra would suggest otherwise.

During the winter 1979 sampling, the fluorescence spectra of three of the five sediment samples collected at the West Hackberry site had peaks corresponding to 376 and 397 nm. These peaks are not similar to either the spectra of the pyrolytic aromatic source material discussed in a previous section or aromatic compounds such as anthracene or phenanthrene. The occurrence of these peaks in the 370-400 nm spectral range suggests that the source compound might be a three- or four-ring aromatic hydrocarbon. At present, the source of the peaks is unknown.

Concentrations of aromatic hydrocarbons in surface sediment samples were calculated by using Bunker C oil as a standard. The Bunker C oil (API Reference No. 4) was chosen due to the similarity of

its spectra with spectra of sediment samples. Concentrations of perylene were calculated by using pure perylene as a standard.

The statistical reliability of the sediment sampling procedure was tested during the fall 1978 samplings. During the fall 1978 sampling, both the composite sample and subsamples of each of the four replicate grabs were analyzed at six of the ten sediment stations. The analytical values determined from the pooled sample was compared to the mean value determined from the four replicates using confidence limits calculated from the Student's t-distribution,  $\bar{X} = t \cdot s / n$ , where  $\bar{X}$  is the replicate mean, s the standard deviation and n the number of replicates. With a 95 percent confidence interval, 90 percent (27 of 30) of the pooled sample values are statistically the same as the replicate mean (Table 12). For a 99 percent confidence interval, 100 percent (30 of 30) agree.

The analytical standard error ranges from 20 to 30 percent for the fluorescence values of the sediment samples (Table 12). The standard error of the replicate grab samples falls in the same range. Therefore most of the variability in the analyses results from laboratory procedures and not from sampling techniques or spatial heterogeneity of the bottom sediments.

The fluorescence values of the bottom sediments are remarkably similar among stations at a given site and between seasons (Table 13). The most striking differences are between the West Hackberry and Weeks Island sites. Concentrations of two-, three-, four-, and five-ring aromatics at the West Hackberry site are consistently five times greater than those at the Weeks Island sites.

TABLE 12

POOLING EXPERIMENT - BOTTOM SEDIMENT SPECTROFLUOROMETRIC DATA, OCTOBER 1973  
( $\mu\text{g/g}$  equivalent)

WEST HACKBERRY					
STATION	312 nm	327 nm	342 nm	405 nm	438 nm
02	8.42 (8.2+1.0) <sup>b</sup>	7.76 (7.9+1.1)	6.12 (6.7+1.5)	2.66 (2.8+1.2)	0.040 (0.039+0.012)
08	8.64 (10.8+2.6)	7.84 (10.3+2.2)	6.40 (8.6+1.4)	2.72 (3.2+1.2)	0.067 (0.061+0.021)
14	6.52 (11.1+2.2)	6.10 (10.0+2.3)	5.26 (7.6+2.0)	2.24 (3.3+1.4)	0.051 (0.070+0.011)
WEEKS ISLAND					
02	2.98 (3.5+1.2)	2.48 (2.9+1.0)	1.68 (1.7+0.6)	0.48 (0.7+0.2)	0.012 (0.010+0.005)
08	1.74 (2.5+0.2)	1.60 (2.1+0.2)	1.20 (1.3+0.3)	0.36 (0.4+0.3)	0.009 (0.008+0.003)
14	1.82 (1.3+0.7)	1.58 (1.4+0.4)	1.08 (0.8+0.3)	0.34 (0.2+0.1)	0.008 (0.006+0.003)
ANALYTICAL REPLICATES					
8A <sup>c</sup>	11.5+3.1	10.8+3.1	8.9+2.4	3.6+0.8	0.080+0.015
Pooled	27%	29%	27%	22%	19%

<sup>a</sup>Concentrations expressed in  $\mu\text{g/g}$  of Bunker C oil (API Reference No. 4) with the exception of the 438 nm peak which is expressed as  $\mu\text{g/g}$  of perylene.

<sup>b</sup>Single standard deviation calculated from four sampling/analytical replicates.

<sup>c</sup>Single standard deviation calculated from three analytical replicates.



TABLE 13

SURFACE SEDIMENT SPECTROFLUOROMETRY DATA  
( $\mu\text{g/g}$  equivalents)<sup>a</sup>

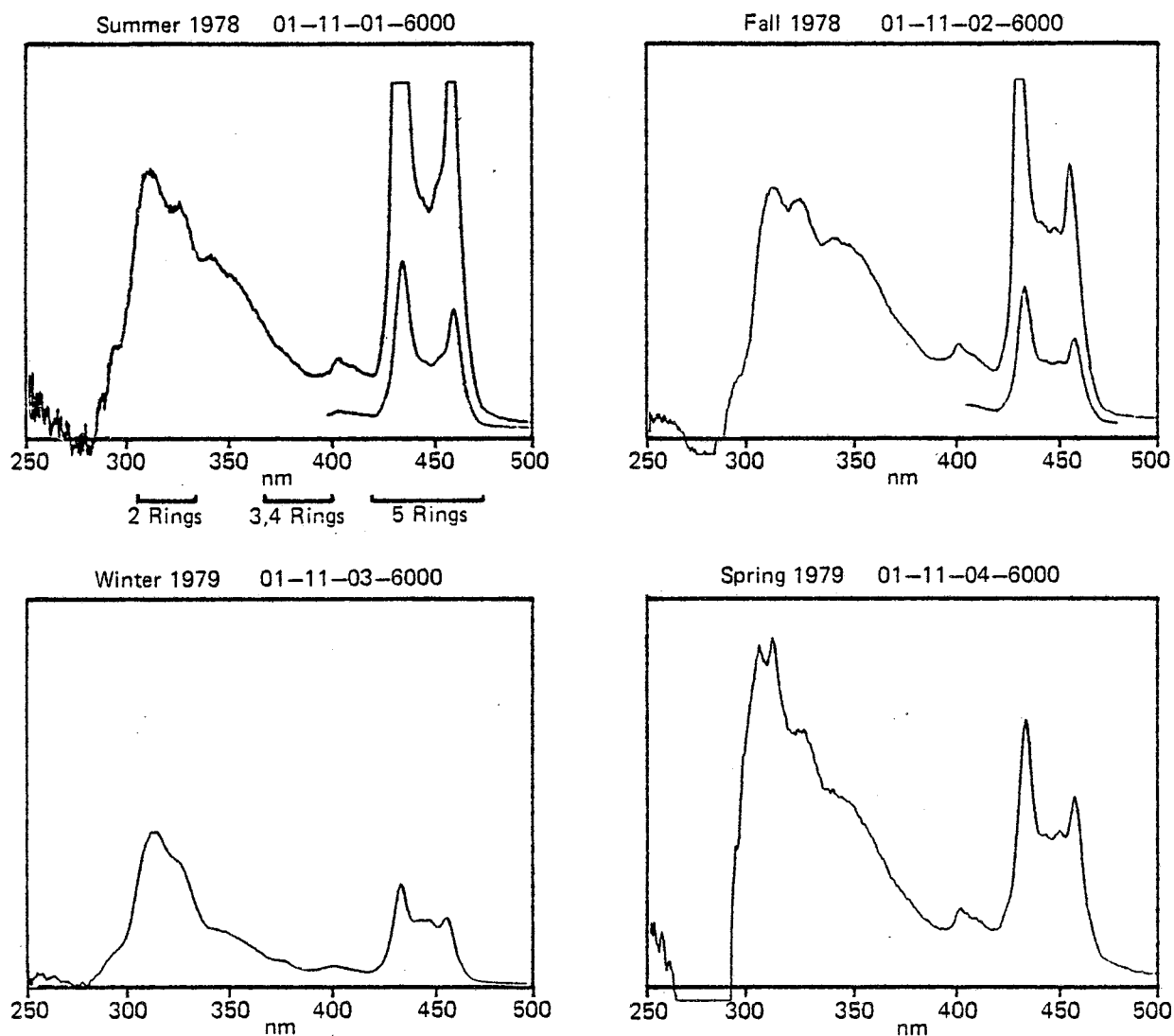
WEST HACKBERRY					
SEASON	312 nm	327 nm	342 nm	405 nm	438 nm
Summer 1978	13.8 $\pm$ 5.1	11.6 $\pm$ 4.1	8.7 $\pm$ 3.0	3.9 $\pm$ 1.3	0.085 $\pm$ 0.028
Fall 1978	9.1 $\pm$ 1.9	8.5 $\pm$ 1.9	7.1 $\pm$ 1.6	3.0 $\pm$ 0.7	0.058 $\pm$ 0.012
Winter 1979	12.3 $\pm$ 17.6 (4.1 $\pm$ 1.4)	11.5 $\pm$ 14.6 (5.1 $\pm$ 2.0)	7.5 $\pm$ 5.8 (5.0 $\pm$ 2.5)	2.9 $\pm$ 1.7 (2.2 $\pm$ 1.0)	0.050 $\pm$ 0.035 (0.036 $\pm$ 0.022)
Spring 1979	19.0 $\pm$ 20.0 (10.4 $\pm$ 5.8)	15.2 $\pm$ 13.7 (9.3 $\pm$ 4.5)	9.6 $\pm$ 5.3 (7.6 $\pm$ 3.0)	3.5 $\pm$ 1.0 (3.3 $\pm$ 1.1)	0.148 $\pm$ 0.204 (0.058 $\pm$ 0.037)
WEEKS ISLAND					
Summer 1979	2.7 $\pm$ 0.5	2.3 $\pm$ 0.4	1.6 $\pm$ 0.5	0.5 $\pm$ 0.2	0.012 $\pm$ 0.006
Fall 1978	2.2 $\pm$ 0.5	1.9 $\pm$ 0.4	1.3 $\pm$ 0.3	0.4 $\pm$ 0.1	0.010 $\pm$ 0.002
Winter 1979	1.6 $\pm$ 1.0	1.5 $\pm$ 1.0	1.2 $\pm$ 0.9	0.5 $\pm$ 0.4	0.007 $\pm$ 0.006
Spring 1979	1.4 $\pm$ 1.0	1.1 $\pm$ 0.9	0.8 $\pm$ 0.6	0.3 $\pm$ 0.2	0.012 $\pm$ 0.014

<sup>a</sup>Concentrations expressed in  $\mu\text{g/g}$  of Bunker C oil (API Reference No. 4) with the exception of the 438 nm peak which is expressed as  $\mu\text{g/g}$  of perylene.

<sup>b</sup>These values calculated without Station 11 which is a high flier.

The fluorescence data at Station 11 at the West Hackberry site illustrate the utility of spectrofluorometry for detecting an input of petroleum to a given station or site (Figure 25). During the summer 1978 and fall 1979 samplings, the fluorescence-derived concentrations of hydrocarbons in the bottom sediments were consistent with concentrations at other stations within the site (Table 14). The relative amounts of two-ring aromatics (312 nm and 327 nm peaks) and three- and four-ring aromatics (342 nm peak) during the winter and spring 1979 samplings are two to three times greater than during the previous samplings. The enriched aromatic concentrations are the result of contamination of the sediments at the station with a petroleum source containing predominantly two- and three-ring aromatics. At present, the source of the contamination is not known.

The aromatic contamination is not evident from the glass capillary gas chromatography data in which aromatic hydrocarbon compositions are obscured by greater concentrations of "interfering" compounds. Since the brine discharge is expected to be enriched in aromatic hydrocarbons, contamination of sediments with hydrocarbons from the brine will be readily detectable. This example illustrates the role that spectrofluorometry with its shorter analysis time, greater sensitivity and lower cost should play in a monitoring program. More detailed analytical techniques might be employed to investigate the nature of the contamination after identification of the problem by spectrofluorometry.



**Analytical Conditions:**

Synchronous Scan: 250-500 nm a 50 nm/min Excitation Offset: -25 nm Mode: A-B (Hexane)  
 Farrand Mark I Instrument with Corrected Excitation and Emission.

Figure 25. Seasonal comparison of fluorescence spectra at Station 11, West Hackberry Site.

TABLE 14

SPECTROFLUOROMETRY DATA FOR BOTTOM SEDIMENTS  
COLLECTED FROM STATION 11, WEST HACKBERRY SITE  
( $\mu\text{g/g}$  equivalents)

STATION 11A					
SEASON	312 nm	327 nm	342 nm	405 nm	438 nm
Summer 1978	15.7	13.8	10.7	4.5	0.116
Fall 1978	10.7	10.2	8.6	3.7	0.063
Winter 1979	43.6	37.4	17.0	5.6	0.103
Spring 1979	53.6	38.8	17.9	4.4	0.509

<sup>a</sup>Concentrations expressed in  $\mu\text{g/g}$  of Bunker C oil (API Reference No. 4) with the exception of the 438 nm peak which is expressed as  $\mu\text{g/g}$  of perylene.

### 3.2.3 Hydrocarbon versus Sedimentological Parameters

In a depositional environment where the sediment geochemistry is determined by "normal" inputs of geochemicals (biological, background pollutant inputs (chronic), terrestrial runoff, atmospheric fallout, etc.) rather than sporadic acute inputs of pollutants, the distribution of these geochemicals will be a function of physical forcing: mixing, transport resuspension, etc.<sup>a</sup> Boehm (1978a,b) and Boehm and Quinn (1978) showed that recent geochemical provinces are described by a mixing line at one end of which is source material having a characteristic mixture of hydrocarbon content and total organic carbon, i.e., a constant ratio of hydrocarbon to TOC, and at the other end material which contains very low levels of hydrocarbons (trace quantities). The mixing of two end members, or the distribution of the former over the region, should yield a regression line defining the natural population. By virtue of the fact that hydrocarbon levels are three orders of magnitude lower than TOC levels, changes can occur in THC levels without influencing the much larger TOC levels to a significant extent. For example, if an aberrant input of hydrocarbons were to occur and THC levels tripled, the corresponding effect on TOC would be 0.3 percent. Thus the THC/TOC ratio as defined by the regression line is a very sensitive indicator of "nonnormal" inputs of hydrocarbons and can serve as a predictor of expected sediment population geochemical contents.

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<sup>a</sup>Natural populations of sediment from a given geochemical "province" will tend to maintain fairly constant ratios of inorganic and organic chemicals. Shokes (1977) has shown this for trace metal distributions.

Such a relationship is shown in Figure 26 for actual THC and TOC data from the West Hackberry and Weeks Island sites. Note the two regions on the graph, corresponding to the two sites. The West Hackberry sediment contains higher TOC and THC levels than the Weeks Island site. Nevertheless, the regression line continues through the two sets of data. The line has a correlation coefficient of 0.81. The ratio of hydrocarbons to total organic carbon for the region is on the average equal to the slope of the line: 0.0042. This means that 0.42 percent of the TOC is hydrocarbon, a very small amount. The remaining TOC is presumably other lipids, humic material, plant pigments, carbohydrates, etc.

Any deviation from this line can be construed as having resulted from an aberrant environmental cause (e.g., pollution, hurricane, etc.) wherein the natural sediment organic composition is changed. A combination of this consideration with full evaluation of composition as revealed by the GC run can be used to evaluate causes of any changes in the hydrocarbon geochemistry.

### 3.3 Macrofaunal Hydrocarbons (Penaeus Sp.)

#### 3.3.1 Hydrocarbon Concentrations

Hydrocarbon concentrations in Penaeus setiferous (white shrimp) samples from West Hackberry and Penaeus aztecus (brown shrimp), Penaeus setiferous and Trachypenaeus samples from Weeks island are presented in Figures 27 and 28. Concentrations of hydrocarbons in Penaeus are determined from GC runs (resolved plus UCM) rather than gravimetrically. Gravimetric results obtained from weighing hydrocarbon extracts on a microbalance often agree well with GC quantifications if large amounts

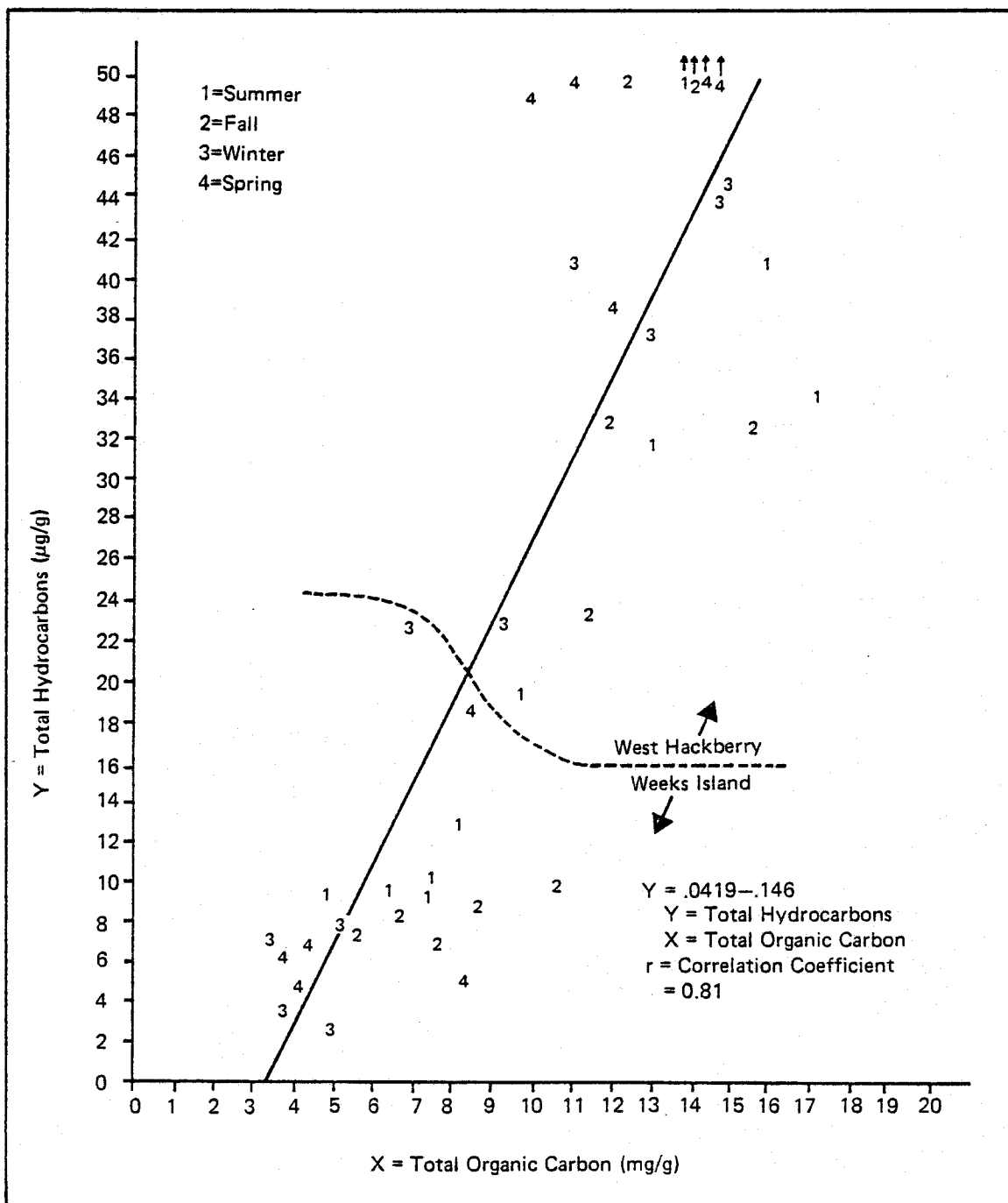


Figure 26. Total hydrocarbon concentration in surface sediment as a function of total organic carbon content.

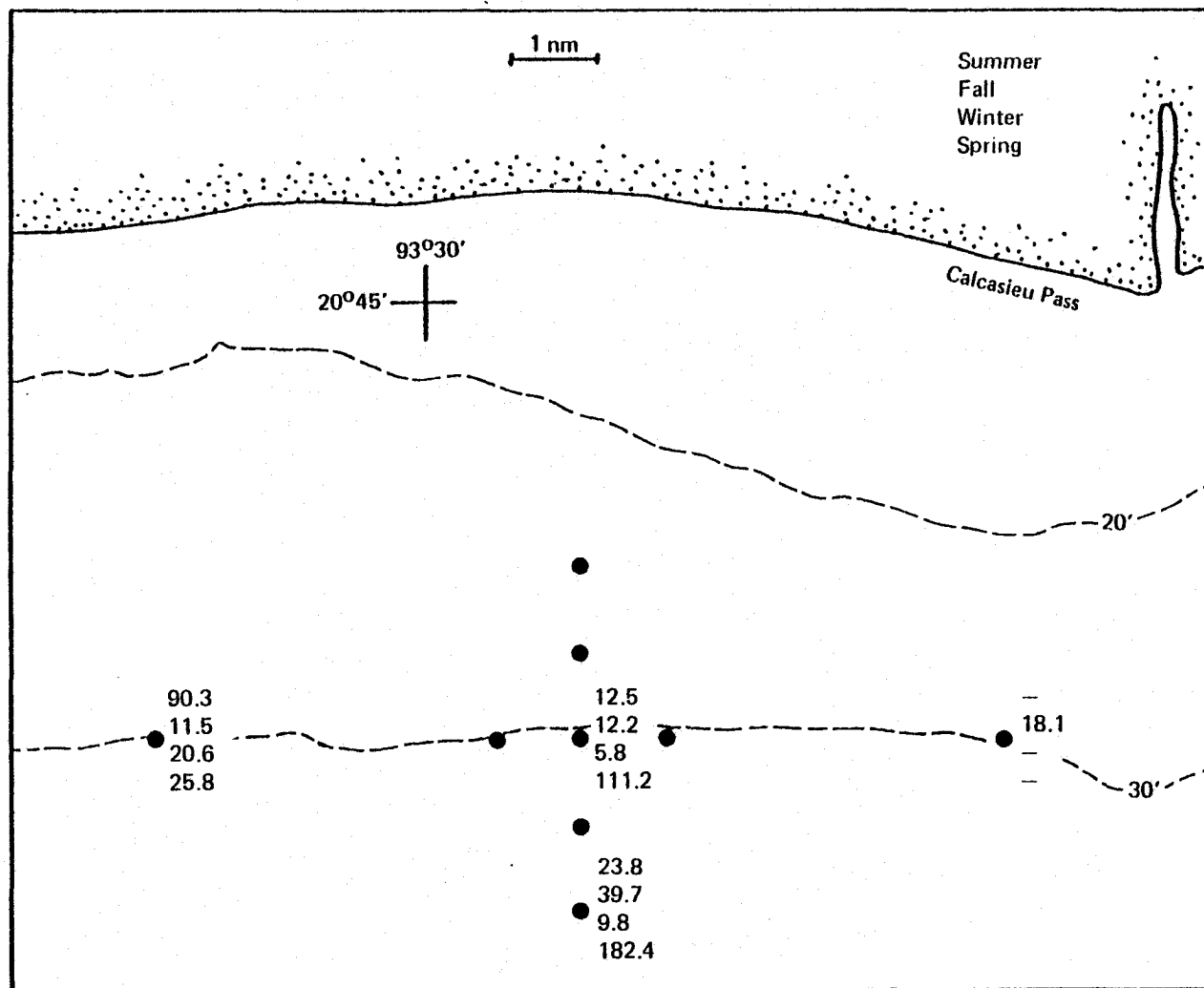


Figure 27. Macrofaunal Hydrocarbon Concentrations, *Penaeus setiferus*, West Hackberry Site ( $\mu\text{g/g}$  dry weight).



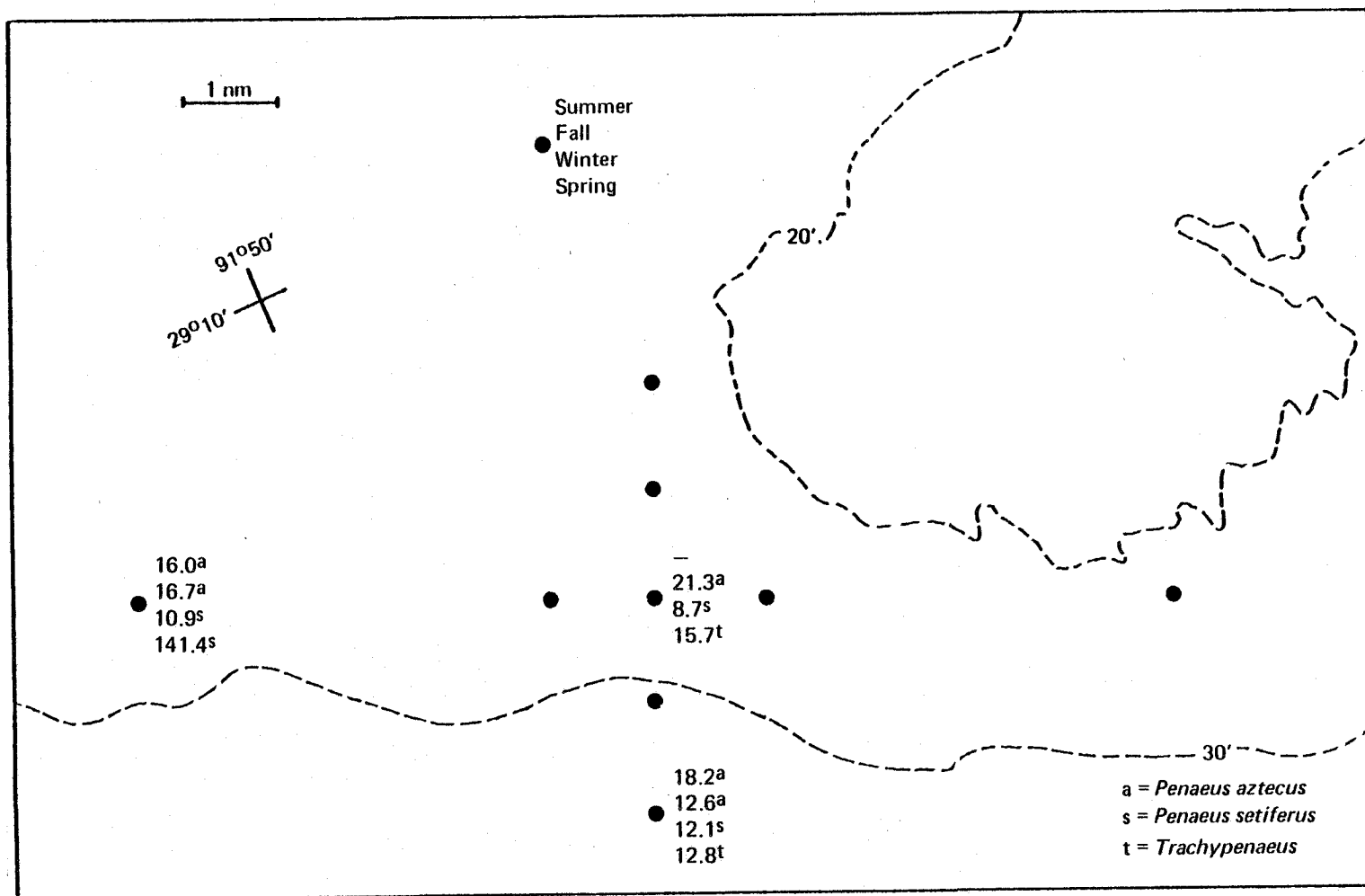


Figure 28. Macrofaunal Hydrocarbon Concentrations, Weeks Island site ( $\mu\text{g/g}$  dry weight).

of biolipids are not present as is the case with most seawater and sediment samples. The biolipids which are not analyzable by GC potentially contain many high molecular weight non-hydrocarbon compounds. Therefore, gravimetric results can be misleading and are not reproducible. Thus, we report all animal tissue hydrocarbon levels as GC determined concentrations (resolved plus unresolved envelope).

Hydrocarbon concentrations in P. setiferous are more or less uniform at both sites ranging from 6ppm to 90 ppm ( $\bar{x} = 21.8 \pm 22.5$  ppm;  $n = 13$ ). Several samples (not included in this average) contain upwards of 100 ppm during the spring cruise which may indicate a recent biochemical change in the organisms leading to a great increase in polar lipids and a breakthrough into the hydrocarbon fraction. No petroleum or other non-biogenic inputs are suggested by their GC traces (see next section).

A limited number of P. aztecus samples ( $n = 5$ ) exhibit uniform hydrocarbon concentrations ( $\bar{x} 17.0 \pm 3.2$  ppm). The two Trachypena samples analyzed average 14.3 ppm.

Thus, on a strict quantitative basis, all macrofaunal samples, other than the ones suspected of containing nonhydrocarbon material, contain between 6 and 90 ppm of hydrocarbons of a mixed source. Concentrations of hydrocarbons reports for P. aztecus collected off the south Texas coast are considerably higher (20-1000  $\mu\text{g/g}$ ) when reported on a dry weight basis (Berryhill, 1975).

During the fall cruise, we performed replicate analyses on both the same sample (homogenate split) and of three separate samples (three individuals each) to determine what the sampling and analytical

TABLE 15

MACROFAUNAL SAMPLING  
AND ANALYTICAL VARIABILITY<sup>a</sup>

---

<u>Site</u>	<u>Station</u>	Concentration ( $\mu\text{g/g}$ )		
		Replicate Number		
		<u>#1</u>	<u>#2</u>	<u>#3</u>
West Hackberry	A8	9.6	13.1	13.8 <u>+</u> 7.4

---

<sup>a</sup>Sampling variability: 12.2+2.3 g/g (+18%)

Analytical variability: 13.8+7.4 g/g (+54%)

variabilities are in determining hydrocarbon concentrations. The results are presented in Table 15. The variability between replicate samples is excellent, having a reproducibility of  $\pm 18$  percent. The analytical variability was greater with a reproducibility of  $\pm 54$  percent which we attribute to nonhomogeneity of the "homogenate" used for this determination. Ideally, the sampling variability is the sum of analytical and sampling uncertainties.

### 3.3.2 Hydrocarbon Composition

#### 3.3.2.1 Gas Chromatography

The sources of the hydrocarbon contents of the macrofauna are revealed by their GC traces. These compositions can be classified into several categories:

B = biosynthesized; characterized by olefinic material (e.g., squalene)

N = smooth n-alkane distribution,  $n\text{-C}_{20}$  to  $n\text{-C}_{34}$ ,  
probably indicative of pelagic tar inputs

U = large unresolved complex mixture indicative of degraded petroleum (i.e. fresh fingerprint lost due to environmental and/or metabolic processes) (U2 = bimodal UCM signifying two petrogenic inputs)

The samples are listed and classified according to this scheme in Table 16. Gas chromatograms illustrating these classes are presented in Figures 29 through 31.

As indicated in Table 16, many of the shrimp samples contain a distribution of hydrocarbons suggesting previous exposure and ingestion of high molecular weight petroleum-derived hydrocarbons. The presence

TABLE 16

SOURCE CLASSIFICATION OF MACROFAUNAL SAMPLES<sup>a</sup>

SPECIES	SITE	STATION	SEASON			
			Summer	Fall	Winter	Spring
<u>P. setiferus</u>	West Hackberry	A2	U/N	B/U	N/U2	B
		A8	N/B	U/B	B	N/U
		A10	N/U	N/U2	N/B	B
		A14	-	N/U2	-	-
	Weeks Island	B2	-	-	N/U	B
		B8	-	-	N/U	-
		B10	N/U/B	-	N/U	-
<u>P. aztecus</u>	Weeks Island	B2	N/B	U2/N	-	-
		B8	-	N/U2	-	-
		B10	B/N	U2/B	-	-
<u>Tracypenaeus</u>	Weeks Island	B2	-	-	-	-
		B8	-	-	-	-
		B10	-	-	-	B/U

<sup>a</sup>See text for explanation of classification system

*Penaeus setiferus* Hydrocarbons  
Spring Cruise (04)  
Station A2—West Hackberry

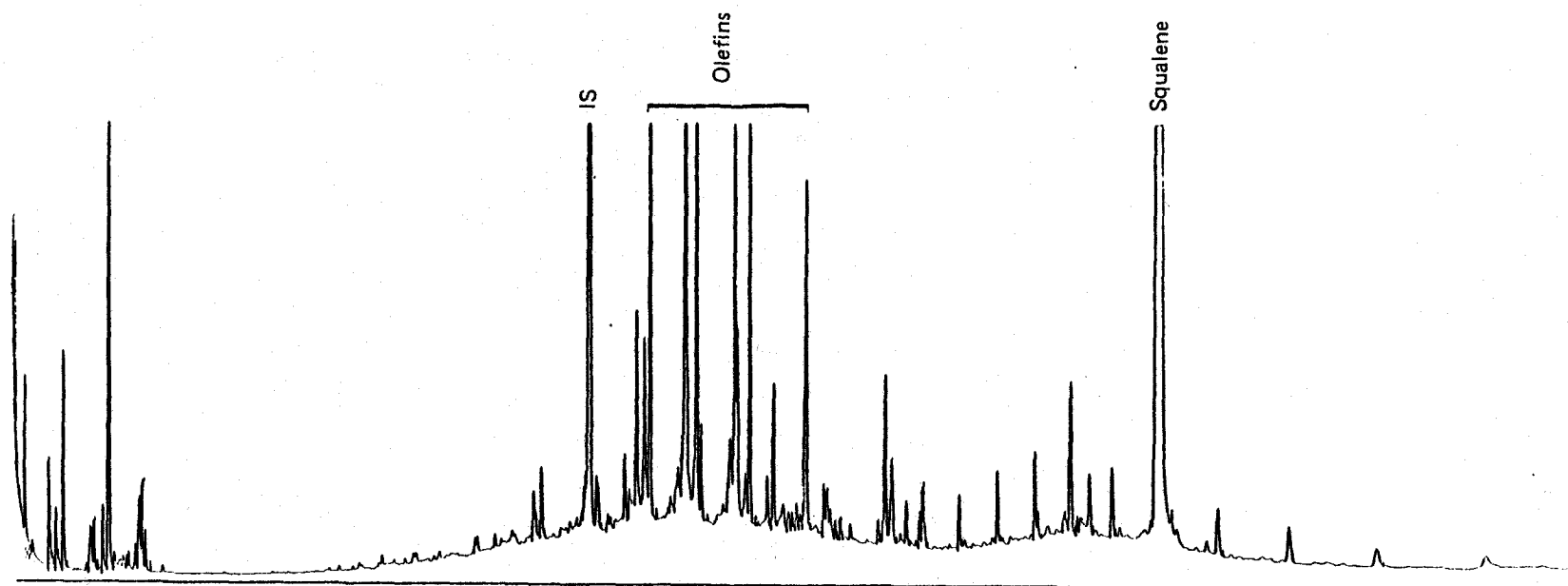


Figure 29. Gas chromatogram of macrofaunal hydrocarbons-Class B.

*Penaeus setiferus* Hydrocarbons  
Fall Cruise (02)  
Station A10—West Hackberry

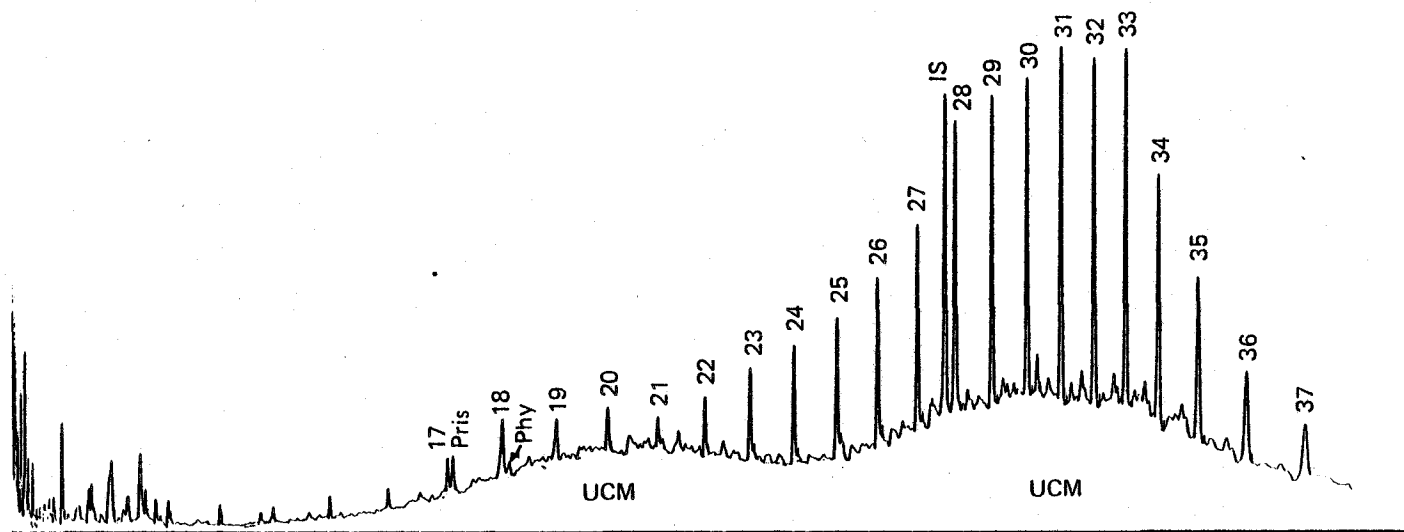


Figure 30. Gas chromatogram of macrofaunal hydrocarbons-Class N/U2.

*Penaeus setiferus* Hydrocarbons  
Winter Cruise (03)  
Station A2—West Hackberry

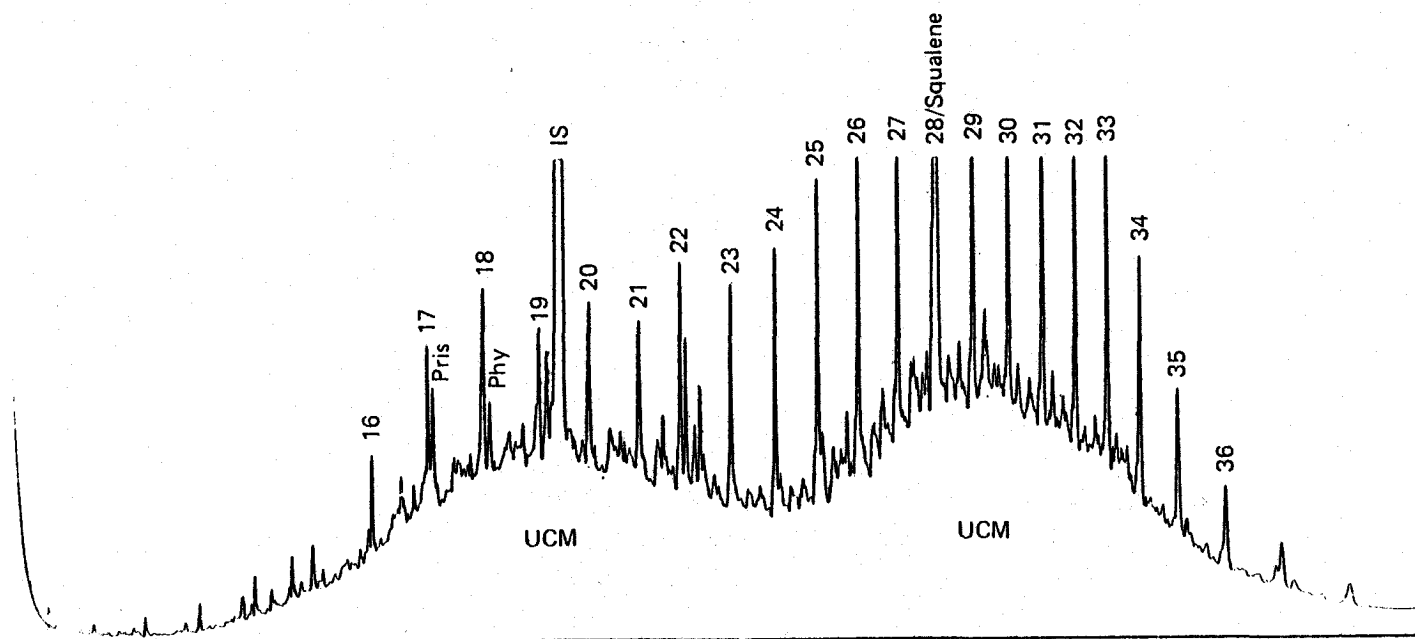


Figure 31. Gas chromatogram of macrofaunal hydrocarbons-Class N/U2.

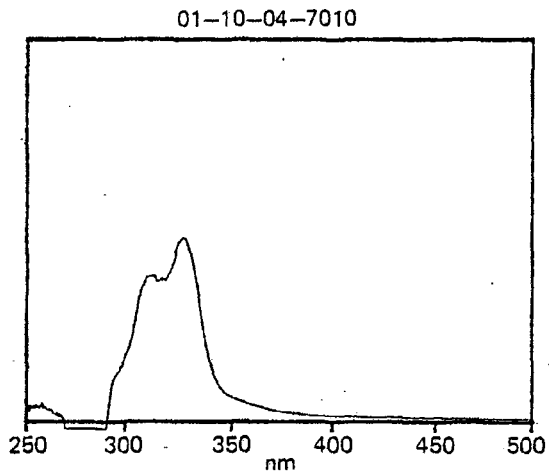
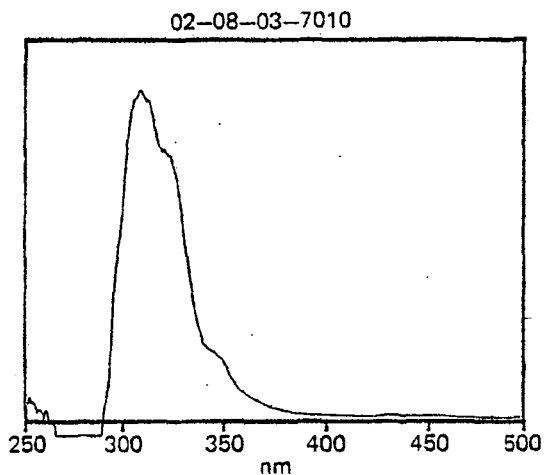
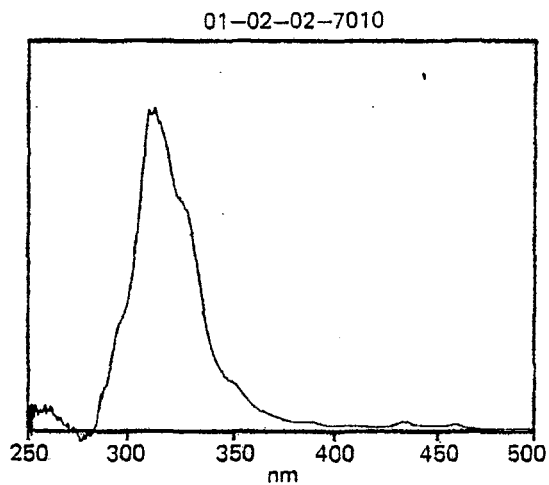
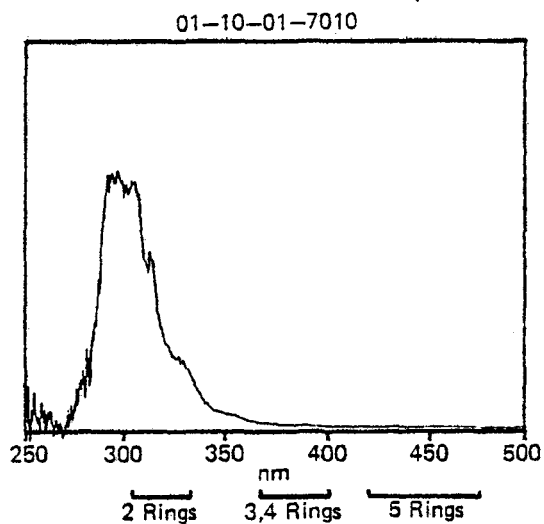


of the UCM (class U) and especially the bimodal (class U2) UCM distribution indicates that shrimp tissue in general from this region contains petroleum hydrocarbons at concentration levels of 10-100 ppm.

#### 3.3.2.2 Macrofauna - UV Spectrofluorometry

The fluorescence spectra of the macrofauna samples are uniformly dominated by a single peak with a maximum at 310 nm (Figure 32). As discussed previously, this spectral type indicates that two-ring aromatics are the predominant aromatics present in the macrofauna samples. This predominance reflects either the composition of the source material or the selective biochemical hydrocarbon uptake and metabolic mechanisms in the shrimp. If shrimp take up aromatics directly from seawater, the selection could be made by the chemical fractionation of two-ring aromatics into the seawater as discussed above.

The concentrations of aromatics in the macrofaunal samples are uniformly low at both the West Hackberry and Weeks Island sites with the exception of the spring 1979 samples (Table 17). Shrimp collected at both sites contain three to five times higher concentrations of aromatic hydrocarbons during the spring 1979 compared to the three previous samplings. The spectra of shrimp collected during the spring 1979 sampling are unique by virtue of the predominance of the 327-nm peak over the 310-nm peak, a reversal compared to previous spectra. The cause of the phenomenon is unknown but could be due to a change in the growth stage of the shrimp or an environmental change possibly related to a change in oceanographic conditions in the vicinity of the two sites.



**Analytical Conditions:**

Synchronous Scan: 250-500 nm @ 50 nm/min    Excitation Offset: -25 nm    Mode: A-B (Hexane)  
 Farrand Mark I Instrument with Corrected Excitation and Emission.

Figure 32. Fluorescence spectra of macrofauna samples.

TABLE 17

MACROFAUNAL SPECTROFLUOROMETRY DATA  
( $\mu\text{g/g}$  equivalents)<sup>a</sup>

WEST HACKBERRY				
SEASON	SPECIES <sup>b</sup>	310 nm	325 nm	348 nm
Summer 1978	S	22.0 $\pm$ 23.7 <sup>c</sup>	4.48 $\pm$ 5.5	0.0
Fall 1978	S	3.2 $\pm$ 3.6	2.0 $\pm$ 2.3	0.0
Winter 1979	S	1.41 $\pm$ 0.3	0.9 $\pm$ 0.3	0.1 $\pm$ 0.2
Spring 1979	S	8.7 $\pm$ 1.4	10.3 $\pm$ 2.6	0.8 $\pm$ 0.8
WEEKS ISLAND				
Summer 1979	A	3.1 $\pm$ 0.1	1.96 $\pm$ 0.02	0.0
Fall 1978	A	2.0 $\pm$ 0.8	1.3 $\pm$ 0.5	0.0
Winter 1979	S	1.01 $\pm$ 0.1	0.8 $\pm$ 0.1	0.1 $\pm$ 0.02
Spring 1979	S	7.8	8.7	1.4
	T	2.07	1.46	0.58
REPLICATES				
Analytical	S	0.60 $\pm$ 0.28	0.12 $\pm$ 0.21	0.0
Sampling	S	0.91 $\pm$ 0.57	0.30 $\pm$ 0.19	0.0

<sup>a</sup>Concentrations expressed as  $\mu\text{g/g}$  of No. 2 fuel oil (API Reference No. 2).

<sup>b</sup>Species S = P. setiferus, Species A = P. aztecus, Species T = Trachypenaeus sp.

<sup>c</sup>Replicate mean of three stations.

### 3.4 Epibenthic Fauna

During the course of this project, three species of benthic epifauna were collected and analyzed for their hydrocarbon content and composition. These animals represent nonmigratory species which are more or less characteristic of a given site. Analyses of these animals is of critical importance to the evaluation of the fate of potentially oily brine. As will be seen, deposit feeding epibenthic organisms will chemically reflect very recent input to the benthic environment and thus may serve as excellent indications of recent chemical changes.

#### 3.4.1 Hydrocarbon Concentrations

Total hydrocarbon concentrations in snails collected at the West Hackberry site during the fall cruise and crabs (Calinectes sapidus and Portunas gebesii) collected at both sites are presented in Figures 33 and 34. Concentrations in the snail tissue ranged from 74.8 to 244.7 ppm; in Calinectes from West Hackberry from 33.4 to 347.0 ppm; in Calinectes from Weeks Island from 34.4 to 721.0 ppm; in Portunas from West Hackberry from 57.9 to 317.1 ppm; in Portunas from Weeks Island from 52.0 to 214.7 ppm. Concentrations are highly variable and exhibit neither seasonal nor spatial trends. Some of the variability is undoubtedly related to feeding behavior which may be linked to unmonitored seasonal changes in the environment.

On several occasions, we examined the sampling variability inherent in epibenthic tissue hydrocarbon measurements. Calinectes sapidus samples were used for these determinations. One sampling

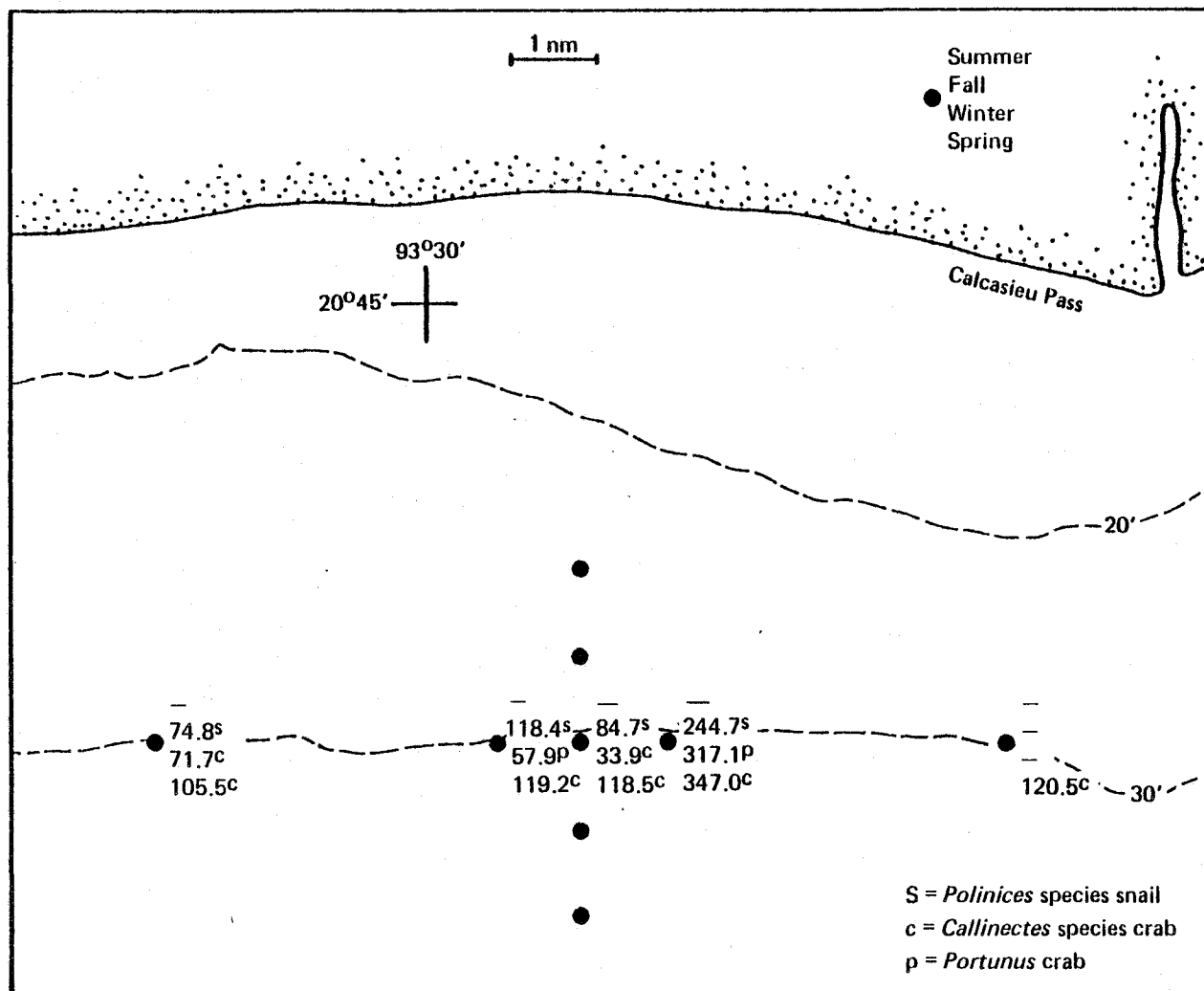


Figure 33. Hydrocarbon Concentrations of benthic epifauna, West Hackberry site ( $\mu\text{g/g}$  dry weight).

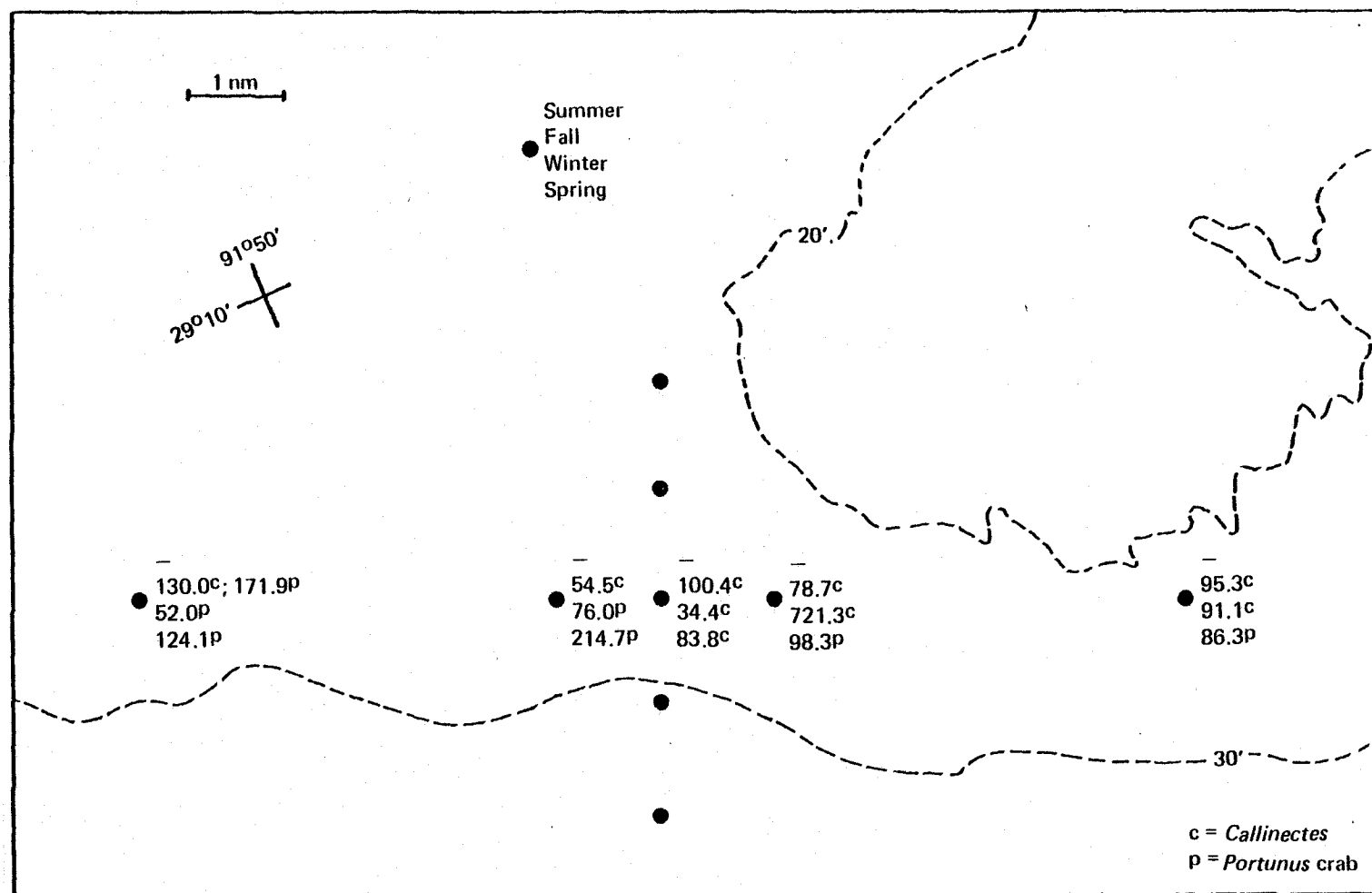


Figure 34. Hydrocarbon Concentrations of benthic epifauna from Weeks Island site ( $\mu\text{g/g}$  dry weight).

from the fall cruise from Weeks Island was split into two samples of five individuals each:  $\bar{x}=54.6 \pm 30.2$  ppm ( $\sigma/\bar{x}=0.5e$ ). The other determination on three samples, twelve individuals each, from West Hackberry (spring) resulted in  $\bar{x} = 382.0 \pm 60.7$ ;  $\sigma/\bar{x} = 0.16$ . The analytical variability on these samples is usually  $\pm 25$  percent. Therefore, the sampling variability ranged from equivalence to the analytical variability (or no detectable sampling variability) to three times the analytical variability.

### 3.4.2 Hydrocarbon Composition

#### 3.4.2.1 Gas Chromatography

GC analyses of epibenthic faunal samples yielded two distinct patterns -- biogenic composition and recent petrogenic composition. Several types of GC traces illustrating petroleum inputs are presented in Figures 35 and 36.

Approximately two-thirds (20) of the samples of Portunus and Calinectes are comprised largely of petroleum hydrocarbons (Figure 35-36). Samples of the snails analyzed in the fall did not exhibit inputs of petroleum. Thus, the concentration levels indicated in Figures 33 and 34 for Calinectes and Portunus can in general be construed as representing nonbiogenic hydrocarbons (i.e., petroleum).

The nature of the petroleum composition is quite interesting and illustrates some fundamental aspects of the hydrocarbon chemistry of the benthos. As mentioned in a previous section, the surface sediment contained hydrocarbons of a land-derived, highly weathered petrogenic distribution. The sediment samples were actually a

*Callinectes sapidus* (Crab) Hydrocarbons  
Spring Cruise (04)  
Station A2—West Hackberry

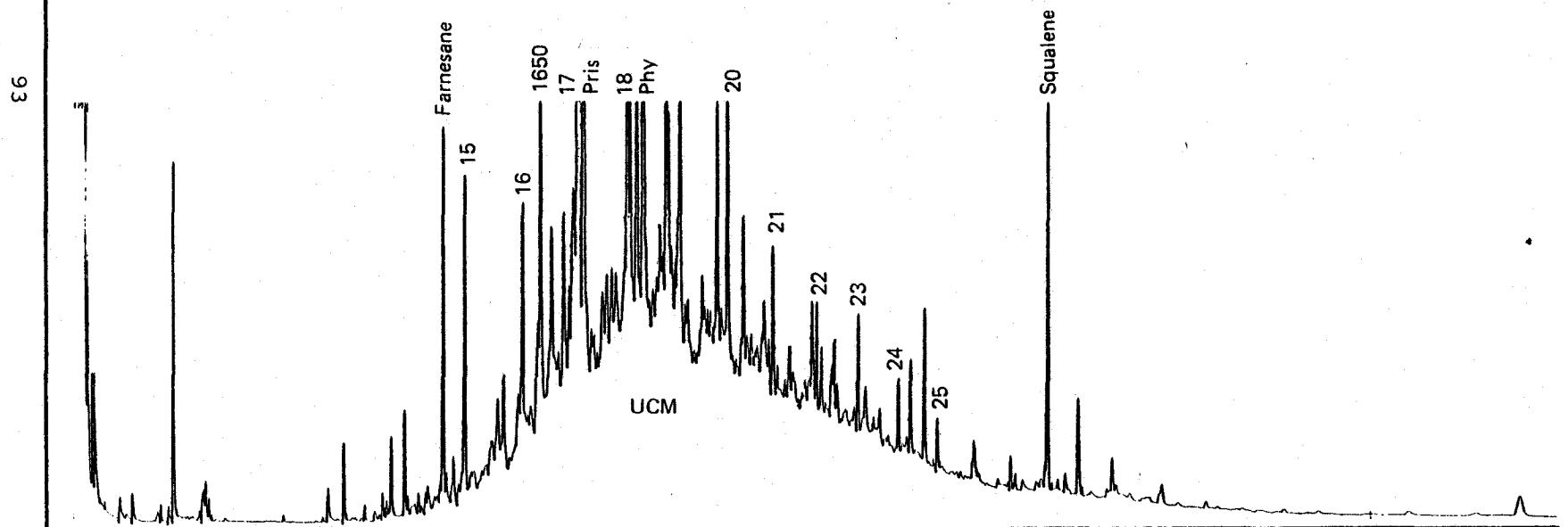


Figure 35. Gas chromatogram of epibenthic fauna-petroleum inputs.



*Portunus gebesii* (Crab) Hydrocarbons  
Spring Cruise (04)  
Station B2—Weeks Island

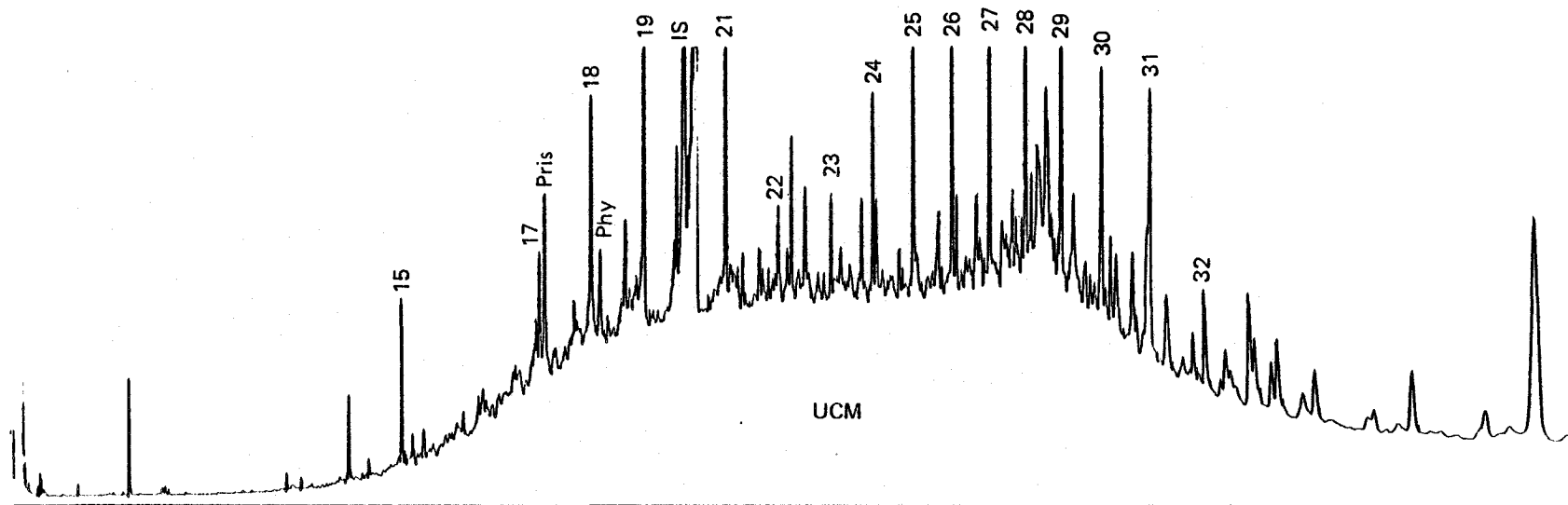


Figure 36. Chromatogram of epibenthic fauna-petroleum inputs.

composite of the top 5 cm of sediment. Teal and Farrington (1977) have shown that surface sediment has a different hydrocarbon composition than the animals residing in or on it. However, deposit feeding benthic epifauna, Calinectes and Portunas, scavenge the very top of the sediment column at the sediment/water interface for their food supply. Their hydrocarbon content and composition then will reflect this very top layer (0-5 mm). GC analysis of their flesh indicates a high petroleum content, apparently unrelated to the bulk sediment composition. Benthic diatoms located at the sediment/water interface have been shown to differ greatly in their hydrocarbon composition relative to surface sediment (0-5 cm) (Thompson and Eglinton, 1976). It should be realized that standard "surface" sediment samples taken from 0-5 cm will greatly "dilute" the composition of the top several millimeters, the site of the most recent pollutant inputs.

The chromatograms are typical of a weathered light petroleum. Similar changes were observed in an oil spill in Sweden (Boehm et al., 1979) where a No. 5 fuel oil weathered very rapidly (microbial degradation) to yield a hydrocarbon assemblage where (1) the n-alkanes were degraded, (2) the isoprenoid hydrocarbons farnesane, pristane and phytane were relatively enhanced on the GC trace due to their relative resistance to microbial degradation and (3) the UCM was enhanced due to degradation of resolved components and possible production of UCM material by microorganisms.

Thus the epibenthic fauna appear to be sensitive indicators of recent pollutant inputs to the benthos and are probably very useful indicators for future changes brought about by offshore post-development activities.

#### 3.4.2.2 Epibenthic Samples - UV Spectrofluorometry

Like the fluorescence spectra of the macrofauna, the spectra of the epibenthic samples are uniformly dominated by a single peak with a maximum at 310 nm (Figure 37). This spectrum results from the predominance of two-ring aromatics in the epibenthic samples. The predominance of the two-ring aromatics could be the result of selective accumulation of enriched source material as discussed in the macrofaunal section.

The concentrations of aromatics in the epibenthic samples show no discernible trends between seasons, stations or sites (Table 18). The large degree of sampling and analytical scatter evident in the replicate data precludes identifying these trends. However, the crab, Portunus gebesii, consistently contains substantially higher concentrations of aromatics relative to the blue crab Calinectes sapidus. This effect may be due to feeding habit or biochemical differences between the species.

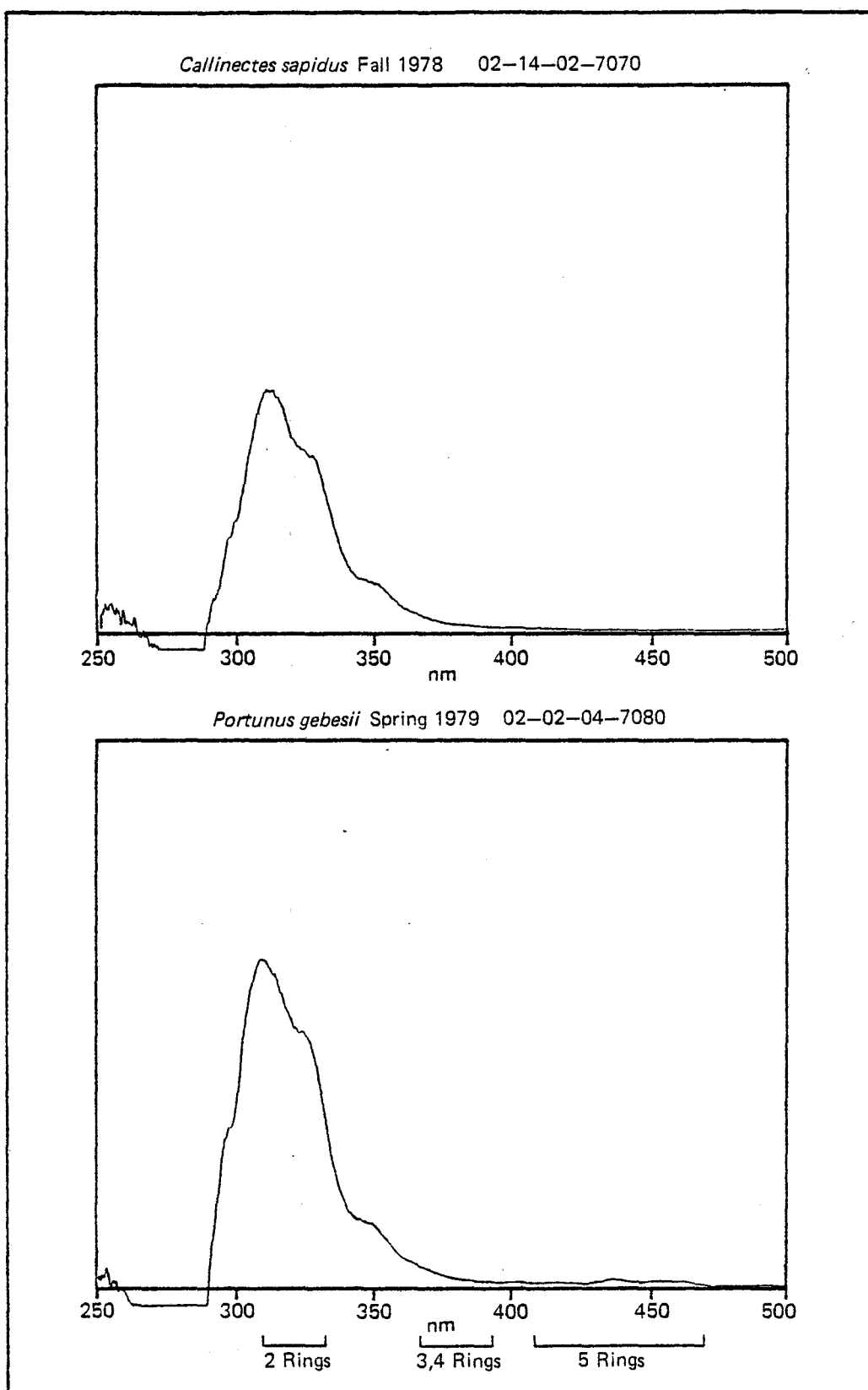


Figure 37. Fluorescence spectra of epibenthic samples.

TABLE 18

SPECTROFLUOROMETRY DATA FOR EPIBENTHIC SAMPLES  
( $\mu\text{g/g}$  equivalents)<sup>a</sup>

WEST HACKBERRY				
SEASON	SPECIES <sup>b</sup>	310 nm	325 nm	349 nm
Summer 1978		No Data		
Fall 1978	S	3.9 $\pm$ 3.2	2.1 $\pm$ 1.5	0.0
Winter 1979	C	2.3 $\pm$ 1.1	1.6 $\pm$ 0.9	0.2 $\pm$ 0.3
	P			
Spring 1979	S	18.7 $\pm$ 20.3	14.0 $\pm$ 15.4	1.1 $\pm$ 1.7
WEEKS ISLAND				
Summer 1979		No Data		
Fall 1978	C	4.3 $\pm$ 3.2	3.1 $\pm$ 2.3	0.0
	P			
Winter 1979	C	2.1 $\pm$ 1.4	1.9 $\pm$ 0.8	0.5 $\pm$ 0.3
	P	4.1 $\pm$ 0.8	3.2 $\pm$ 0.9	0.7 $\pm$ 0.3
Spring 1979	C	2.5	1.8	0.6
	P	8.8 $\pm$ 3.4	6.6 $\pm$ 2.3	1.8 $\pm$ 0.7
REPLICATES				
Analytical	C	2.9 $\pm$ 2.3	2.1 $\pm$ 1.6	0.0
Sampling	C	18.9 $\pm$ 9.7	14.9 $\pm$ 7.5	4.2 $\pm$ 2.1

<sup>a</sup>Concentrations expressed as g/g of No. 2 fuel oil (API Reference No. 2).

<sup>b</sup>Species C = Cancer sapidus, Species P = Portunus gebesii, Species S = Polinectes.

#### 4. Discussion

An overall appraisal of the data previously presented leads to the conclusion that the various components of the ecosystem off the coast of Louisiana are largely uncoupled with respect to their hydrocarbon concentration levels and hydrocarbon compositions. Seawater hydrocarbon concentrations appear to be largely independent of suspended particle concentrations but probably a function of both the dissolved/colloidal concentrations and the nature of the suspended particulates. A single tar particle or zooplankter in 1000 clay particles will profoundly affect the hydrocarbon concentrations and composition. The aromatic hydrocarbon composition of the seawater samples as revealed by UV spectrofluorometry indicates that two-ringed aromatics dominate the samples, thus suggesting that the more water-soluble two-ringed compounds are introduced to the samples in a dissolved form. Concentration differences between the West Hackberry and Weeks Island sites are probably due to localized inputs due to hydrographic factors, adjacent terrestrial, riverine runoff, or ship traffic, rather than to area-wide trends dominated by Mississippi River drainage. The Mississippi influence may have been observed in the winter samples which were of equal concentration at both sites and dominated by petrogenic inputs.

Surface sediment samples, which essentially reflect time-averaged environmental conditions, are largely unrelated directly to seawater composition. Both sites are part of the same geochemical province, and concentrations of hydrocarbons are highly correlated with silt/clay content of the sediment. Both GC and UV-fluorescence analyses indicate that the hydrocarbons in sediments reflect large anthropogenic influences

characterized by degraded petrogenic and pyrolytic compounds. PAH compounds are abundant in sediment and largely absent from most other components of the ecosystem. A notable exception is at station All during the winter and spring seasons where spectrofluorometry revealed a close connection between sedimentary and water column PAH compositions (i.e. the presence of significant quantities of 3-4 ringed aromatics in the water column). This difference was masked by nonfluorescing compounds and was not readily noted by gravimetric or GC analysis.

Animals living and feeding at the sediment water interface (0-5 mm) are comprised of hydrocarbons characteristic of neither the surface sediment (0-3 cm) nor the overlying water. Deposit feeders exhibit tissue hydrocarbon compositions closely resembling weathered light petroleum by GC analyses. Thus, the benthic interface may be a sensitive location of the most recently deposited material entering the food web.

The commercially important macrofaunal (shrimp) samples exhibit varying concentrations and compositions of hydrocarbons ranging from biogenic material to petrogenic hydrocarbons. Both sites are chemically heterogeneous with respect to these migratory animals. The hydrocarbons in these samples, therefore, cannot be categorized on a site basis as spatial and seasonal changes greatly mask an attempt to define baseline hydrocarbon concentrations or compositions.

We are left with the questions: What segments of the marine ecosystem will best reflect changes in the chemical nature of the environment? What methods and techniques should be employed to monitor the possible inputs of hydrocarbon-bearing brines into these segments of the ecosystem?

We have found that it is necessary to measure both the quantitative and qualitative nature of the hydrocarbons in marine samples. Seawater will reflect the short-term changes caused by an environmental perturbation, and it is clear that the UV-spectrofluorometric method is both a sensitive indicator of quantitative differences between samples as well as indicating the nature of aromatic hydrocarbons entering the system. Changes in composition of seawater samples that were revealed by spectrofluorometry could have only been detected by the more expensive technique of GC/MS. Furthermore, the aromatic hydrocarbons are probably the most toxic of the organic chemicals that might be introduced in brine discharges and their close rapid analysis is only possible by UV-spectrofluorometry. We have used this technique on board the R/V Researcher to monitor oil in the water column at the site of the Ixtoc I oilspill on a real-time basis (Fiest and Boehm, unpublished data).

In order to monitor time-averaged chemical changes in the system, surface sediments should be analyzed. However, a great effort should be made to sample scrutinize the top 0-1 cm as this represents the most recent (months to years) inputs. The most thorough way to monitor changes would be the combined use of the ratio approach wherein deviations from the well-established total hydrocarbon:total organic carbon regression are measured. Inputs of pollutant materials will cause perturbations from the natural population of sediment defined by the THC/TOC ratio. Gravimetric results can be used for hydrocarbon measurements in conjunction with spectrofluorometric measurements. Where fluorometry detects a suspected change in PAH composition, glass



capillary GC can be brought into play to define any changes in detail and examine the cause of the change.

The data generated in this study suggest that animals living and feeding at the sediment/water interface may reflect the most recent anthropogenic inputs into the benthic system. A combination of analyses of surface sediment, epibenthic deposit feeders and sediment trap samples form a powerful trio in detecting recent additions of pollutants to the sensitive benthic communities. Sediment traps will capture material being sedimented out of the water column and epibenthic animals will reflect the extent of biological assimilation of this material. The traps form the powerful link between the water column and benthic systems heretofore overlooked in monitoring studies in all but a few studies (e.g., Boehm et al., 1979).

This study has indicated that segments of the marine ecosystem are quite compartmentalized with respect to their hydrocarbon chemistry and has revealed that analytical methodology based on a carefully chosen combination of gravimetric analyses, UV-spectrofluoremetric and GC analyses backed by a minimum of GC/MS work has defined the hydrocarbon chemistry of the brine disposal sites off Louisiana and can be used in future offshore monitoring programs for assessing environmental chemical changes.

## 5. Conclusions

1. Hydrocarbon levels in seawater in the region generally range from 6 to 80 ppb. Levels are higher during all seasons at the West Hackberry site. Compositions reflect a composite input of biogenic and petrogenic hydrocarbons, the latter being most abundant in the winter. Two-ringed aromatic hydrocarbons dominate the fluorescence spectra.
2. Hydrocarbon concentrations in surface sediment at the West Hackberry stations are 2-5 times higher than those at Weeks Island. The differences can be attributed to the sediment texture with finer sediment containing higher hydrocarbon levels. The compositions at both sites are identical, being dominated by weathered petrogenic inputs. Both sites are part of the same geochemical province (same source material). Hydrocarbon levels at both sites are highly correlated with organic carbon levels. Aromatic hydrocarbons are introduced by a combination of petrogenic and pyrolytic sources.
3. Macrofaunal (shrimp) concentrations of hydrocarbons are quite similar at both sites showing little spatial or seasonal trends. Hydrocarbon profiles are dominated by a mixture of biogenic and pelagic tar inputs.
4. Epibenthic animals (crabs) consistently reveal hydrocarbon compositions indicative of weathered light petroleum. Distributions are unlike those of seawater or bulk sediment. Hydrocarbons in epibenthic animals probably reflect material at the sediment/water interface.
5. A combination of gravimetric, UV-fluorometric, gas chromatographic and GC/MS analyses (in descending order of usage) is recommended for use in future monitoring studies. Perturbations in sediment contaminants can be followed through monitoring of the changes in the total hydrocarbon/total organic carbon ratio. The validation of this monitoring tool is based on the assumption that the predominant sources of sediment to the site, the two end-members of the mixing curve, do not change. Observations over the one year study period indicate that these sediments are remarkably homogeneous and fall close to the mixing curve for the THC/TOC ratio.

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## APPENDIX A

### SUMMARY OF SAMPLES COLLECTED BY SEASON

HYDROCARBON SAMPLE INVENTORY  
SUMMER 1978

SITE	SAMPLE TYPE	STATION NO.	LATITUDE	LONGITUDE	WATER DEPTH	DATE	TIME	COMPOSITE SAMPLES	REPLICATE SAMPLES
West Hackberry	Bottom Sediment	A2	29° 39.76'	93° 33.78'	Bottom	27 June 78	1115	1	
		A5	39.90'	29.16'	Bottom	26 June 78	1815	1	
		A8	40.00'	28.00'	Bottom	27 June 78	0815	1	
		A11	40.06'	26.90'	Bottom	26 June 78	1405	1	
		A14	40.33'	22.29'	Bottom	23 June 78	2140	1	
	Macrocrustacean ( <i>Penaeus setiferus</i> )	A2	29° 39.76'	93° 33.78'	Bottom trawl	20 June 78	0030	1	
		A8	40.00'	28.00'	Bottom trawl	19 June 78	0505	1	
			38.00'	27.86'	Bottom trawl	19 June 78	2249	1	
	Water Samples (10 liters)	A2			4.0 m	27 June 78	1050		1
		A5			4.0 m	26 June 78	1735		1
		A8			3.5 m	27 June 78	0805		1
		A11			4.0 m	26 June 78	1335		1
		A14			4.0 m	26 June 78	0830		1
	Benthic	None collected; no living specimens at this site.							
Weeks Island	Bottom sediment	B2	29° 07.97'	91° 52.71'	Bottom	28 June 78	0800	1	
		B5	06.15'	48.62'	Bottom	28 June 78	1035	1	
		B8	05.70'	47.60'	Bottom	28 June 78	1410	1	
		B11	05.28'	46.54'	Bottom	28 June 78	1905	1	
		B14	03.43'	42.21'	Bottom	29 June 78	1205	1	
	Macrocrustacean ( <i>Penaeus aztecus</i> )	B2	29° 07.97'	91° 52.71'	Bottom trawl	21 June 78	2331	1	
		B10	03.91'	46.54'	Bottom trawl	21 June 78	2146	1	
	Water samples (10 liters)	B2			4.0 m	28 June 78	0745		1
		B5			3.0 m	28 June 78	1000		1
		B8			3.0 m	28 June 78	1845		1
		B11			3.5 m	28 June 78	1335		1
		B14			2.0 m	29 June 78	1150		1
	Benthic species <sup>a</sup>	snail	B2		Bottom dredge	29 June 78	1600	1	
		snail	B5		Bottom dredge	29 June 78	1500	1	
		starfish	B5		Bottom dredge	29 June 78	1500	1	
		starfish	B8		Bottom dredge	29 June 78	1440	1	
		hermit crab	B8		Bottom dredge	29 June 78	1440	1	
		starfish	B11		Bottom dredge	29 June 78	1415	1	
		starfish	B14		Bottom dredge	29 June 78	1235	1	
		snail	B14		Bottom dredge	29 June 78	1235	1	

<sup>a</sup> These samples were destroyed by a power failure and were not analyzed.

HYDROCARBON SAMPLE INVENTORY  
FALL 1978

SITE	SAMPLE TYPE	STATION NO.	LATITUDE	LONGITUDE	WATER DEPTH	DATE	TIME	COMPOSITE SAMPLES	REPLICATE SAMPLES	POOLING EXPT
West Hackberry	Bottom Sediment	A2	29°39.76'	93°33.78'	Bottom	12 Oct. 78	2150	1		4
		A5	39.90'	29.16'	Bottom	12 Oct. 78	2040	1		
		A8	40.00'	28.00'	Bottom	12 Oct. 78	1920	1		4
		A11	40.06'	26.90'	Bottom	3 Oct. 78	1200	1		
		A14	40.33'	22.29'	Bottom	3 Oct. 78	1115	1		4
	Macrocrustacean <sup>a</sup> ( <u>Penaeus setiferus</u> )	A2	29°39.76'	93°33.78'	Bottom trawl	29 Sep. 78	0103	1		
		A8	40.00'	28.00'	Bottom trawl	26 Sep. 78	2277	1	2	
		A10	38.00'	27.86'	Bottom trawl	28 Sep. 78	2014	1		
	Water samples (10 liters)	A2			Mid-depth	12 Oct. 78	2140	1		
		A5			Mid-depth	12 Oct. 78	2025	1	2	
		A8			Mid-depth	12 Oct. 78	1915	1		
		A11			Mid-depth	3 Oct. 78	1150	1		
		A14			Mid-depth	3 Oct. 78	1045	1		
	Benthic species (snails)	A2			Blake trawl	29 Sep. 78	1625	1		
		A5			Blake trawl	29 Sep. 78	1740	1	1 <sup>b</sup>	
		A8			Blake trawl	29 Sep. 78	1910	1		
		A11			Blake trawl	29 Sep. 78	2100	1		
		A14			Blake trawl	29 Sep. 78	2300	1		
Weeks Island	Bottom Sediment	B2	29°07.97'	91°52.71'	Bottom	9 Nov. 78	1240	1		4
		B5	06.15'	48.62'	Bottom	9 Nov. 78	1430	1		
		B8	05.70'	47.60'	Bottom	10 Nov. 78	0740	1		4
		B11	05.28'	46.54'	Bottom	10 Nov. 78	1140	1		
		B14	03.43'	42.21'	Bottom	10 Nov. 78	1330	1		4
	Macrocrustacean ( <u>Penaeus aztecus</u> )	B2	29°07.97'	91°52.71'	Bottom trawl	30 Sep. 78	1939	1		
		B8			Bottom trawl	1 Oct. 78	0030	1	2	
		B10	03.91'	46.54'	Bottom trawl	1 Oct. 78	0205	1		
	Water samples (10 liters)	B2			Mid-depth	9 Nov. 78	1220	1		
		B5			Mid-depth	9 Nov. 78	1405	1	2	
		B8			Mid-depth	10 Nov. 78	0720	1		
		B11			Mid-depth	10 Nov. 78	1120	1		
		B14			Mid-depth	10 Nov. 78	1320	1		
	Benthic species (Blue crabs)	B2			Bottom trawl	30 Sep. 78	1939	1		
		B5			Bottom trawl	1 Oct. 78	1745	1	2	
		B8			Bottom trawl	1 Oct. 78	0035	1		
		B11			Bottom trawl	1 Oct. 78	1600	1		
		B14			Bottom trawl	1 Oct. 78	0414	1		

<sup>a</sup>One additional sample of Penaeus was collected at Station 14.

<sup>b</sup>One replicate not collected.



HYDROCARBON SAMPLE INVENTORY  
WINTER 1979

SITE	SAMPLE TYPE	STATION NO.	LATITUDE	LONGITUDE	WATER DEPTH	DATE	TIME	COMPOSITE SAMPLES	REPLICATE SAMPLES
Weeks Island	Bottom Sediment (Top 3 centimeters)	B2	29°07.97'	91°52.71'	Bottom	28 Jan. 79	1000	1	
		B5	29°06.15'	91°48.62'	Bottom	28 Jan. 79	0840	1	
		B8	29°05.70'	91°47.60'	Bottom	27 Jan. 79	1740	1	
		B11	29°05.28'	91°46.54'	Bottom	27 Jan. 79	1110	1	
		B14	29°03.43'	91°42.21'	Bottom	27 Jan. 79	0910	1	
	Macrocrustacean ( <i>Penaeus setiferus</i> )	B2	29°07.97'	91°52.71'	Bottom trawl	16 Jan. 79	2241	1	
		B8	29°05.70'	91°47.60'	Bottom trawl	17 Jan. 79	0211	1	
		B10	29°03.91'	91°46.54'	Bottom trawl	17 Jan. 79	2225	1	
	Benthic Species (Blue Crab)								
		<i>P. gebesii</i> B2			Bottom trawl	16 Jan. 79	2241	1	
		<i>P. gebesii</i> B5			Bottom trawl	18 Jan. 79	0059	1	
		<i>C. sapidus</i> B8			Bottom trawl	17 Jan. 79	0348	1	
		<i>C. sapidus</i> B11			Bottom trawl	18 Jan. 79	0005	1	
		<i>C. sapidus</i> B14			Bottom trawl	17 Jan. 79	1913	1	
	Seawater (10 liters)	B2			Mid-depth	28 Jan. 79	1010		1
		B5			Mid-depth	28 Jan. 79	0830		1
		B8			Mid-depth	27 Jan. 79	1730		1
		B11			Mid-depth	27 Jan. 79	1100		1
		B14			Mid-depth	27 Jan. 79	0900		1
West Hackberry	Bottom Sediment (Top 3 centimeters)	A2	29°39.76'	93°33.78'	Bottom	25 Jan. 79	0915	1	
		A5	29°39.90'	93°29.16'	Bottom	25 Jan. 79	1200	1	
		A8	29°40.00'	93°28.00'	Bottom	25 Jan. 79	2100	1	
		A11	29°40.06'	93°26.90'	Bottom	26 Jan. 79	1110	1	
		A14	29°40.33'	93°22.29'	Bottom	26 Jan. 79	1310	1	
	Macrocrustacean ( <i>Penaeus setiferus</i> )	A2	29°39.76'	93°33.78'	Bottom trawl	15 Jan. 79	2151	1	
		A8	29°40.00'	93°28.00'	Bottom trawl	15 Jan. 79	0232	1	
		A10	29°38.00'	93°27.86'	Bottom trawl	15 Jan. 79	0426	1	
	Benthic Species								
		<i>C. sapidus</i> A2			Bottom trawl	15 Jan. 79	2151	1	
		<i>P. gebesii</i> A5			Bottom trawl	15 Jan. 79	2327	1	
		<i>C. sapidus</i> A8			Bottom trawl	15 Jan. 79	0232	1	
		<i>P. gebesii</i> A11			Bottom trawl	16 Jan. 79	0100	1	
		— A14			Bottom trawl	14 Jan. 79	2041	N.S. <sup>a</sup>	
	Seawater (10 liters)	A2			Mid-depth	25 Jan. 79	0855		1
		A5			Mid-depth	25 Jan. 79	1150		1
		A8			Mid-depth	25 Jan. 79	2100		1
		A11			Mid-depth	26 Jan. 79	1100		1
		A14			Mid-depth	26 Jan. 79	1300		1

<sup>a</sup>No crabs could be collected at this site.

HYDROCARBON SAMPLE INVENTORY  
SPRING 1979

SITE	SAMPLE TYPE	STATION NO.	LATITUDE	LONGITUDE	WATER DEPTH	DATE	TIME	COMPOSITE SAMPLES	REPLICATE SAMPLES
West Hackberry	Bottom Sediment	A2	29° 39.76'	93° 33.78'		2 May 79		1	
		A5	29° 39.90'	93° 29.16'		2 May 79		1	
		A8	29° 40.00'	93° 28.00'		2 May 79		1	
		A11	29° 40.06'	93° 26.90'		1 May 79		1	
		A14	29° 40.33'	93° 22.29'		1 May 79		1	
	Macrocrustacean (shrimp)								
	White shrimp	A2	29° 39.76'	93° 33.78'		16 Apr. 79	1938	1	
	White shrimp	A8	29° 40.06'	93° 26.90'		16 Apr. 79	0135	1	
	White shrimp	A10	29° 38'	93° 27.86'		17 Apr. 79	2121	1	
	Benthic Species (crabs)								
	<u>C. sapidus</u>	A2	29° 39.76'	93° 33.78'		16 Apr. 79	1938	1	
	<u>C. sapidus</u>	A5	29° 39.90'	93° 29.16'		17 Apr. 79	1847	1	
	<u>C. sapidus</u>	A8	29° 40.00'	93° 26.90'		16 Apr. 79	0135	1	
	<u>C. sapidus</u>	A11	29° 40.06'	93° 26.90'		17 Apr. 79	1936	1	
	<u>C. sapidus</u>	A14	29° 38.08'	93° 32.10'		18 Apr. 79	0023	1	
	Seawater	A2	29° 39.76'	93° 33.78'	Mid-depth	2 May 79			1
		A5	29° 39.90'	93° 29.16'	Mid-depth	2 May 79			1
		A8	29° 40.00'	93° 26.90'	Mid-depth	2 May 79			1
		A11	29° 40.06'	93° 26.90'	Mid-depth	1 May 79			1
		A14	29° 40.33'	93° 22.29'	Mid-depth	1 May 79			1
Weeks Island	Bottom Sediment	B2	29° 07.97'	91° 52.71'		30 Apr. 79	2130	1	
		B5	29° 06.15'	91° 48.62'		30 Apr. 79	2030	1	
		B8	29° 05.70'	91° 47.60'		30 Apr. 79	1530	1	
		B11	29° 05.28'	91° 46.54'		30 Apr. 79	1045	1	
		B14	29° 03.43'	91° 42.21'		30 Apr. 79	0830	1	
	Macrocrustacean (shrimp)								
	White shrimp	B2	29° 7.97'	91° 52.71'		18 Apr. 79	1932	1	
	<u>Trachypenaeus</u>	B8	29° 5.70'	91° 47.60'		18 Apr. 79	0042	1	
	<u>Trachypenaeus</u>	B10	29° 3.91'	91° 48.62'		19 Apr. 79	1921	1	
	Benthic Species (crabs)								
	<u>P. gebesii</u>	B2	29° 7.97'	91° 52.71'		18 Apr. 79	1932	1	
	<u>P. gebesii</u>	B5	29° 6.15'	91° 48.62'		21 Apr. 79	0515	1	
	<u>C. sapidus</u>	B8	29° 5.70'	91° 47.60'		18 Apr. 79	0113	1	
	<u>P. gebesii</u>	B11	29° 5.9'	91° 46.4'		20 Apr. 79	0320	1	
	<u>P. gebesii</u>	B14	29° 3.43'	91° 42.21'		20 Apr. 79	0108	1	
	Seawater	B2	29° 07.97'	91° 52.71'	Mid-depth	30 Apr. 79	2115		1
		B5	29° 06.15'	91° 48.62'	Mid-depth	30 Apr. 79	2015		1
		B8	29° 05.70'	91° 47.60'	Mid-depth	30 Apr. 79	1515		1
		B11	29° 05.28'	91° 46.54'	Mid-depth	30 Apr. 79	1030		1
		B14	29° 03.43'	91° 42.21'	Mid-depth	30 Apr. 79	0815		1

## APPENDIX B

### SUMMARY DATA TABLES

# EXPLANATION OF APPENDIX B DATA TABLES

## Capline ID:

Sample ID Format: 00-00-00-0000  
Site-Station-Cruise-Sample Type

Site Key: 01 Texoma (West Hackberry) Site A  
02 Capline (Weeks Island) Site B

Station Key: Stations numbered according to  
NOAA/NMFS specifications.

Cruise Key: June, 1978 01  
October, 1978 02  
January, 1979 03  
April, 1979 04

Sample Type Key: 6000 Bottom Sediments  
3000 Water Samples  
7000 Organisms  
7010 Penaeus setiferus  
7030 Penaeus aztecus  
7060 Polinices sp. (snails)  
7070 Callinectes sapidus (blue crab)  
7080 Portunus gebesii  
7090 Trachypenaeus sp. (shrimp)

Fourth digit of sample type is the replicate  
number. 0 = composite sample, 1,2,3,... = replicates

Blanks have an ID with the station designated  
to be 99 and a sample type ID beginning with  
a digit 9.

9600 = sediment blank  
9700 = organism blank  
9300 = water blank

If more than one blank for a particular sample type  
is processed during a single season, consecutive  
station numbers are assigned to each blank.

Dry Weight: Dry weight of the sample used for the analysis (grams).

Species Code: See sample type key above.

# Individuals: Number of individuals used for the analyses.

EXPLANATION OF APPENDIX B DATA TABLES (CONT.)

$f_{1/2}$  GC ( $\mu\text{g/g}$ ) Total: Concentration of total  $f_1 + f_2$  hydrocarbons as measured by glass capillary gas chromatography

$f_{1/2}$  GC ( $\mu\text{g/g}$ ) Unresolved: Concentration of total  $f_1 + f_2$  hydrocarbons present as an unresolved complex mixture as measured by glass capillary gas chromatography

$f_{1/2}$  GC ( $\mu\text{g/g}$ ) Resolved: Concentration of  $f_1 + f_2$  hydrocarbons present in resolved peaks as measured by glass capillary gas chromatography

$f_{1/2}$  Grav ( $\mu\text{g/g}$ ) Total: Concentration of total  $f_1 + f_2$  hydrocarbons as measured by gravimetry on a Cahn Electro-balance

CPI: Carbon Preference Index

$$\text{CPI} = \frac{2 \times (\text{nC27} + \text{nC29})}{\text{nC26} + 2 \times \text{nC28} + \text{nC30}}$$

Individual Hydrocarbons: Concentration of hydrocarbons with these retention indices as determined by the internal standard method of quantification using androstane.

1500 = nC15

1708 = pristane

2800 = nC28 + squalene

2900 = nC29

(see text for additional information)

UV Fluorescence Peaks: Concentration of hydrocarbons based on peak height measurements made at the used wavelength. Concentrations are expressed as  $\mu\text{g/g}$  equivalents of API No. 2 fuel oil. Different response factors were used for each sample type.

Water  $R_f = 1.0$

Tissues  $R_f = 1.0$

Sediment  $R_f = 2.0$  with the exception of the 438 nm peak  $R_f = .0075$ .

(see text for additional information)

CAPLINE ID	Dry Weight (g)					INDIVIDUAL HYDROCARBONS (ng/g)				
		f <sub>1/2</sub> GC (ug/g) Total	f <sub>1/2</sub> GC (ug/g) Unresolved	f <sub>1/2</sub> GC (ug/g) Resolved	f <sub>1/2</sub> Grav (ug/g) Total	CPI	1708/1700	1500	1708	2900
01-02-01-6000	52.20	34.07	32.55	1.52	34.47	1.60	0.83	69.34	17.35	89.91
01-05-01-6000	50.30	36.92	35.20	1.72	32.03	0.92	1.66	92.47	44.25	113.55
01-08-01-6000	43.60	66.03	62.66	3.37	50.05	1.53	1.28	107.30	50.60	97.90
01-11-01-6000	42.40	39.30	37.41	1.89	40.99	1.34	1.19	78.85	32.07	111.70
01-14-01-6000	73.90	24.90	24.13	0.77	19.21	3.27	0.88	69.19	30.21	38.38
02-02-01-6000	77.70	13.61	13.21	0.40	10.20	0.77	2.00	26.88	20.46	12.48
02-05-01-6000	69.20	14.23	13.80	0.43	9.54	0.56	1.28	22.57	11.40	15.91
02-08-01-6000	73.30	14.23	13.61	0.62	12.69	0.68	1.10	50.71	13.74	20.91
02-11-01-6000	84.80	14.04	13.59	0.45	9.43	0.65	0.86	19.67	8.11	21.57
02-14-01-6000	72.70	11.74	11.40	0.34	9.49	0.20	1.04	18.83	4.91	4.85
99-01-01-9600	50.00	0.36	0.00	0.36	1.00	0.00	0.00	0.00	0.00	0.00
99-01-01-9600	100.00	0.01	0.00	0.01	0.20	0.00	0.00	0.00	0.00	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEDIMENT SAMPLES JUNE 1978

CAPLINE ID	Dry Weight (g)	INDIVIDUAL HYDROCARBONS (ng/g)										
		f <sub>1/2</sub> GC (µg/g) Total	f <sub>1/2</sub> GC (µg/g) Unresolved	f <sub>1/2</sub> GC (µg/g) Resolved	f <sub>1/2</sub> GRAV (µg/g) Total	CPI	1708/1700	1500	1708	2086	2800	2900
01-02-02-6000	51.80	21.56	20.02	1.54	32.60	0.56	0.49	141.40	25.90	258.00	92.40	39.20
01-02-02-6001	63.60	25.17	24.30	0.87	23.30	1.53	0.65	6.70	3.30	43.90	49.50	60.70
01-02-02-6002	54.90	35.95	33.80	2.15	38.10	0.95	1.32	4.20	6.70	405.30	168.40	123.00
01-02-02-6003	62.40	50.79	48.00	2.79	44.70	1.03	0.00	10.60	1.50	283.00	190.10	194.10
01-02-02-6004	60.40	21.67	20.12	0.00	35.70	1.21	0.00	8.10	0.00	406.20	105.60	121.70
01-05-02-6000	36.70	42.17	38.28	3.89	64.80	0.85	1.26	39.80	29.20	837.40	293.70	189.30
01-08-02-6000	44.60	34.70	32.48	2.22	33.20	0.49	1.04	33.80	29.00	500.30	168.40	99.20
01-08-02-6000-2	39.30	45.70	42.61	3.09	60.00	1.11	1.61	44.70	40.90	455.00	125.90	110.00
01-08-02-6000-3	59.30	25.78	23.56	2.22	29.00	1.06	1.34	36.60	24.40	271.50	85.90	69.70
01-08-02-6001	37.20	57.69	54.30	3.39	59.70	0.94	1.52	28.50	25.40	778.20	264.10	187.80
01-08-02-6002	74.20	27.51	25.72	1.79	30.80	1.26	1.14	21.50	16.80	509.80	70.70	69.50
01-08-02-6003	61.00	49.79	46.35	3.44	58.50	0.73	1.36	0.00	21.30	712.40	250.50	172.90
01-08-02-6004	46.20	48.50	46.00	2.50	45.90	1.03	1.13	30.30	18.00	499.90	180.20	145.90
01-11-02-6000	59.40	42.54	39.60	2.94	52.50	0.69	1.13	21.70	19.90	363.10	229.90	203.20
01-14-02-6000	66.20	13.77	12.92	0.85	23.60	0.89	0.78	33.50	13.00	119.01	56.20	44.60
01-14-02-6001	62.70	33.51	32.00	1.51	33.20	1.38	1.58	7.90	9.70	252.10	120.70	118.00
01-14-02-6002	57.30	24.14	22.90	1.24	24.80	1.57	1.35	15.40	18.60	125.30	24.50	72.80
01-14-02-6003	50.60	20.40	18.90	1.50	49.80	1.64	0.74	14.30	7.20	95.40	55.20	83.80
01-14-02-6004	47.00	20.82	19.70	1.12	49.30	1.80	0.92	14.50	9.30	171.80	57.50	91.00
02-02-02-6000	111.50	2.49	2.30	0.19	9.80	0.82	1.20	3.80	3.10	28.40	7.90	6.40
02-02-02-6001	133.20	6.67	6.29	0.38	8.40	0.57	1.02	5.80	5.80	40.50	36.40	16.80
02-02-02-6002	90.50	9.58	7.64	1.94	8.50	0.54	0.96	5.80	6.30	75.50	54.50	22.50
02-02-02-6003	103.00	9.05	8.51	0.54	8.80	0.56	0.98	6.90	8.40	73.60	43.00	18.80
02-02-02-6004	90.80	25.15	23.70	1.45	19.40	1.00	1.34	28.90	24.70	224.30	60.10	65.30
02-05-02-6000	107.50	7.58	6.85	0.73	6.70	0.67	1.03	18.00	11.50	102.80	67.20	35.80
02-08-02-6000	112.60	6.83	6.40	0.43	6.90	0.86	0.96	5.80	5.50	94.99	30.40	21.10
02-08-02-6001	74.30	15.26	14.60	0.66	12.00	0.71	1.02	9.40	12.20	172.80	60.40	28.00
02-08-02-6002	86.90	5.65	5.00	0.65	8.10	0.79	0.93	9.80	7.40	87.00	64.00	37.50
02-08-02-6003	91.10	15.56	14.93	0.63	12.10	1.06	0.80	10.80	8.20	124.90	29.30	26.20
02-08-02-6004	87.80	7.57	7.14	0.43	8.00	1.08	0.99	6.70	9.00	91.34	23.40	19.70
02-11-02-6000	120.40	7.56	7.01	0.55	8.60	0.50	1.71	11.30	14.40	101.84	55.70	21.80
02-14-02-6000	101.70	6.20	5.43	0.77	8.10	0.49	0.64	28.50	12.90	81.46	48.90	15.40
02-14-02-6001	103.30	2.26	1.78	0.48	4.06	0.35	0.77	5.40	7.00	33.80	52.60	12.10
02-14-02-6002	97.10	4.25	3.24	1.01	4.43	0.23	0.83	3.80	2.70	37.10	56.10	8.50
02-14-02-6003	95.50	7.64	6.98	0.66	9.80	2.41	0.91	31.20	27.50	35.47	5.70	11.00
02-14-02-6004	96.10	7.80	7.14	0.66	6.80	0.47	0.73	21.20	17.10	111.31	45.70	15.20
99-01-02-9600	50.00	0.00	0.00	0.00	3.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00
99-02-02-9600	50.00	3.50	0.00	3.50	0.00	0.00	0.00	0.00	0.00	0.00	2.10	0.00
99-03-02-9600	50.00	0.00	0.00	0.00	1.60	0.00	0.00	0.00	0.00	0.00	1.00	0.00

CAPLINE ID	Dry Weight (g)						INDIVIDUAL HYDROCARBONS (ng/g)					
		f <sub>1/2</sub> GC (µg/g) Total	f <sub>1/2</sub> GC (µg/g) Unresolved	f <sub>1/2</sub> GC (µg/g) Resolved	f <sub>1/2</sub> GRAV (µg/g) Total	CPI	1708/1700	1500	1708	2086	2800	2900
01-02-03-6000	88.00	21.93	21.01	0.92	23.12	1.00	2.79	14.90	21.07	29.71	56.43	44.98
01-05-03-6000	40.22	30.01	28.90	1.11	37.51	14.91	0.94	18.03	13.19	309.95	3.89	49.24
01-08-03-6000	38.43	44.02	41.48	2.54	87.01	0.81	1.61	33.16	325.51	277.15	139.74	103.63
01-11-03-6000	39.81	44.84	42.47	2.37	78.38	0.94	1.69	44.07	28.08	277.70	162.97	116.05
01-14-03-6000	48.92	41.02	38.98	2.04	80.74	2.04	1.27	24.93	20.31	133.46	87.63	174.30
02-02-03-6000	72.44	7.53	7.12	0.41	6.54	0.94	1.39	3.73	4.09	10.50	39.49	29.97
02-05-03-6000	80.44	72.05	60.85	11.20	2.68	0.64	1.08	42.40	36.60	0.00	65.61	574.22
02-08-03-6000	69.46	7.84	7.54	0.30	7.69	0.77	1.34	3.25	6.92	0.00	42.65	23.92
02-11-03-6000	76.57	2.18	2.12	0.06	22.92	0.68	0.00	0.00	0.00	0.00	0.00	18.93
02-14-03-6000	90.86	2.51	2.13	0.38	3.67	0.49	0.86	7.20	2.50	12.70	25.40	8.00
99-01-03-9600	100.00	33.84	26.94	6.90	0.32	0.00	0.00	0.00	0.00	0.00	86.05	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEDIMENT SAMPLES JANUARY 1979



CAPLINE ID	Dry Weight (g)						INDIVIDUAL HYDROCARBON					
		f <sub>1/2</sub> GC (µg/g) Total	f <sub>1/2</sub> GC (µg/g) Unresolved	f <sub>1/2</sub> GC (µg/g) Resolved	f <sub>1/2</sub> GRAV (µg/g) Total	CPI	1708/1700	1500	1708	2086	2800	2900
01-02-04-6000	58.10	35.71	33.31	2.40	38.64	6.56	2.80	20.44	37.24	175.00	70.00	122.65
01-05-04-6000	56.80	45.06	41.16	3.90	49.01	1.56	3.68	38.37	86.39	214.55	141.80	95.28
01-08-04-6000	50.00	56.02	51.86	4.16	59.16	5.83	23.71	43.54	71.32	175.39	140.00	144.29
01-11-04-6000	52.00	82.37	79.63	2.74	68.60	0.73	3.81	24.45	80.24	137.84	163.50	76.68
01-14-04-6000	53.10	36.45	33.09	3.36	52.27	4.46	2.19	33.50	71.76	101.39	89.50	84.16
02-02-04-6000	89.00	19.51	18.43	1.08	18.77	2.20	2.21	10.60	28.04	41.34	51.00	42.16
02-05-04-6000	84.80	3.79	3.49	0.30	4.47	3.95	0.95	2.33	2.79	12.00	23.30	9.65
02-06-04-6000	84.00	4.23	3.88	0.35	4.88	0.75	1.39	6.99	6.25	3.06	19.90	11.65
02-11-04-6000	72.60	3.22	2.80	0.42	6.57	3.31	5.68	2.18	16.08	39.52	16.60	6.96
02-14-04-6000	74.40	3.44	3.01	0.43	5.96	0.46	1.84	1.92	7.27	36.00	16.36	5.24
99-01-04-9600	67.50	0.27	0.22	0.05	1.07	0.00	0.00	0.00	1.52	0.00	0.00	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEAWATER SAMPLES, May 1979.

CAPLINE ID	Volume (l)	INDIVIDUAL HYDROCARBONS (ng/g)											
		f <sub>1</sub> /2 GC (µg/g)	f <sub>1</sub> /2 GC (µg/g)	f <sub>1</sub> /2 GC (µg/g)	f <sub>1</sub> /2 GRAV (µg/g)	CPI	1708/1700	1300	1500	1708	2028	2800	2900
01-02-01-3001	10.00	6.22	5.61	0.61	5.10	0.00	0.41	0.00	53.07	11.48	88.93	132.81	0.00
01-05-01-3001	10.00	3.59	2.58	1.01	3.60	0.00	0.13	11.73	511.39	6.77	60.80	32.20	0.00
01-08-01-3001	10.00	7.37	6.09	1.28	17.10	0.00	0.34	85.28	324.08	8.43	185.09	70.99	0.00
01-11-01-3001	10.00	22.69	20.60	2.09	30.00	0.00	0.08	133.06	1164.83	9.16	63.58	45.80	0.00
01-14-01-3001	10.00	9.33	7.87	1.46	14.50	0.00	0.16	13.75	384.45	6.77	280.92	39.95	22.49
02-02-01-3001	10.00	4.91	3.59	1.32	7.10	0.00	0.50	44.84	79.26	22.52	37.58	14.31	0.00
02-05-01-3001	10.00	8.15	7.00	1.15	8.40	0.00	2.33	152.97	293.17	49.54	34.66	112.39	4.19
02-08-01-3001	10.00	5.11	4.45	0.66	5.00	0.00	2.08	14.75	305.85	35.52	8.02	50.59	5.09
02-11-01-3001	10.00	0.42	0.00	0.42	6.80	0.00	0.81	0.00	298.15	19.92	24.29	10.11	0.00
02-14-01-3001	10.00	2.45	2.09	0.36	3.80	0.00	0.69	0.00	91.24	20.23	45.81	42.86	3.94
99-01-01-9300	10.00	6.48	6.43	0.07	6.00	0.00	0.00	0.00	0.00	0.00	0.00	26.15	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEAWATER SAMPLES JUNE 1978

CAPLINE ID	Volume (l)							INDIVIDUAL HYDROCARBONS (ng/g)					
		f <sub>1</sub> /2 GC (µg/g) Total	f <sub>1</sub> /2 GC (µg/g) Unresolved	f <sub>1</sub> /2 GC (µg/g) Resolved	f <sub>1</sub> /2 GRAV (µg/g) Total	CPI	1708/1700	1300	1500	1708	2028	2800	2900
01-02-02-3001	10.00	2.89	0.97	1.92	14.00	0.00	0.00	32.90	1085.50	8.90	31.60	12.70	8.90
01-05-02-3001	10.00	5.02	2.02	3.00	18.00	0.00	0.00	110.20	2004.00	13.70	32.50	21.10	16.30
01-05-02-3002	10.00	8.01	5.60	2.41	16.00	0.00	0.00	3.00	1836.00	0.00	24.20	23.80	21.90
01-05-02-3003	10.00	17.50	14.00	3.50	76.00	0.00	0.00	3.40	1011.00	0.00	0.00	7.80	0.00
01-08-02-3001	10.00	3.48	2.66	0.82	12.00	0.00	0.00	0.00	459.70	4.50	60.70	23.50	9.50
01-11-02-3001	10.00	77.68	63.40	14.28	86.00	0.00	0.00	84.80	1150.00	1548.40	19.30	27.50	0.00
01-14-02-3001	10.00	6.70	6.03	0.67	16.00	0.00	0.00	0.00	0.00	0.00	22.50	63.40	42.00
02-02-02-3001	10.00	8.56	7.76	0.80	7.70	0.00	0.00	5.60	162.70	6.50	116.10	79.80	34.70
02-05-02-3001	10.00	3.82	3.34	0.48	5.30	0.00	0.00	0.00	38.10	0.00	351.80	0.00	0.00
02-05-02-3002	10.00	1.18	0.69	0.49	5.80	0.00	0.00	1.40	122.10	0.00	119.50	31.70	7.20
02-05-02-3003	10.00	1.91	1.45	0.46	6.20	0.00	0.00	8.40	73.20	2.50	110.50	39.20	0.00
02-08-02-3001	10.00	3.95	3.51	0.44	7.10	0.00	0.00	17.50	58.90	2.40	73.60	41.40	0.00
02-11-02-3001	10.00	2.62	2.30	0.32	8.00	0.00	0.00	5.20	72.40	1.20	97.20	24.90	4.90
02-14-02-3001	10.00	1.62	1.20	0.42	10.00	0.00	0.00	0.00	52.20	0.00	185.50	65.50	19.70
99-01-02-9300	10.00	0.19	0.00	0.19	1.00	0.00	0.00	0.00	0.00	0.00	0.00	9.10	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEAWATER SAMPLES OCTOBER 1978

CAPLINE ID	Volume (l)	INDIVIDUAL HYDROCARBONS (ng/g)											
		f <sub>1/2</sub> GC (µg/g)	f <sub>1/2</sub> GC (µg/g)	f <sub>1/2</sub> GC (µg/g)	f <sub>1/2</sub> GRAV (µg/g)	CPI	1708/1700	1300	1500	1708	2028	2800	2900
01-02-03-3001	10.00	24.04	22.05	1.99	29.30	0.87	0.12	3.10	65.50	7.40	108.40	198.40	138.20
01-05-03-3001	10.00	5.18	4.57	0.61	10.60	0.96	0.27	0.60	11.30	7.80	40.60	34.80	26.70
01-08-03-3001	10.00	7.25	6.16	1.09	16.10	1.00	0.12	7.80	35.60	5.40	102.40	80.50	65.40
01-11-03-3001	10.00	8.94	8.22	0.72	6.40	0.99	0.29	0.00	8.30	5.50	89.00	62.80	50.90
01-14-03-3001	10.00	13.68	11.50	2.18	27.80	0.99	0.13	0.00	132.70	27.50	37.00	61.50	50.10
02-02-03-3001	10.00	6.43	5.21	1.22	6.40	1.12	0.00	113.20	29.70	0.00	42.40	23.40	20.80
02-05-03-3001	10.00	8.50	6.10	2.40	4.60	1.03	0.55	146.20	48.50	5.80	48.70	69.00	80.40
02-08-03-3001	10.00	2.77	2.22	0.55	2.20	0.46	0.00	6.10	17.60	80.00	37.90	47.40	13.30
02-11-03-3001	10.00	4.08	3.70	0.38	12.50	1.00	0.27	2.10	8.70	3.00	4.60	23.40	31.00
02-14-03-3001	10.00	5.87	5.01	0.86	5.80	0.78	0.27	8.60	30.10	8.60	55.60	54.20	33.80
99-01-03-3001	10.00	0.05	0.05	0.00	2.00	0.00	0.00	0.00	0.00	0.00	0.00	2.60	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEAWATER SAMPLES JANUARY 1979

CAPLINE ID	Volume (l)	f <sub>1/2</sub> GC (µg/g) Total	f <sub>1/2</sub> GC (µg/g) Unresolved	f <sub>1/2</sub> GC (µg/g) Resolved	f <sub>1/2</sub> GRAV (µg/g) Total	CPI	INDIVIDUAL HYDROCARBONS (ng/g)						
							1708/1700	1300	1500	1708	2028	2800	2900
01-02-04-3000	10.00	6.87	3.96	2.81	24.23	2.00	0.45	2.00	13.00	17.00	46.00	1433.00	36.00
01-05-04-3000	10.00	8.49	6.70	1.79	21.26	2.11	0.38	0.00	14.06	13.50	55.00	762.70	13.92
01-08-04-3000	10.00	7.29	6.56	0.73	5.40	0.09	0.40	0.00	23.88	5.94	106.20	269.42	6.46
01-11-04-3000	10.00	9.21	8.08	1.13	10.65	0.57	0.39	0.00	19.14	10.87	113.70	113.81	40.53
01-14-04-3000	10.00	10.54	8.42	2.12	13.81	1.21	0.56	0.00	12.34	16.66	193.80	911.80	28.14
02-02-04-3000	10.00	4.21	3.81	0.40	2.50	0.35	1.00	0.00	18.46	10.60	16.70	54.31	7.57
02-05-04-3000	10.00	22.01	19.60	2.41	16.22	0.82	0.69	4.92	188.00	51.59	71.10	262.60	94.31
02-08-04-3000	10.00	0.69	0.63	0.06	1.71	1.04	0.00	0.00	1.68	1.10	3.52	14.40	1.56
02-11-04-3000	10.00	12.31	10.82	1.49	26.00	1.71	0.58	3.58	104.40	38.73	54.20	134.40	39.34
02-14-04-3000	10.00	20.97	18.19	2.78	21.90	1.19	0.77	7.19	101.52	78.23	14.00	243.30	135.73
99-02-04-9300	0.00	0.01	0.00	0.01	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

CAPLINE REPORT: HYDROCARBON ANALYSIS OF SEAWATER SAMPLES, May 1979

CAPLINE ID	Dry Weight	Species Code	# Individuals	f <sub>1/2</sub> GC (µg/g)				CPI	INDIVIDUAL HYDROCARBONS (ng/g)			
				Total	Unresolved	Resolved	Total		1500	1708	2800	2900
01-02-01-7010	17.00	1.	4.	90.28	76.01	14.27	68.30	0.68	16.24	23.01	980.35	670.52
01-08-01-7010	24.40	1.	4.	12.50	7.14	5.36	175.30	0.50	9.10	0.00	457.70	357.88
01-10-01-7010	14.50	1.	2.	23.85	17.68	6.17	47.68	0.76	0.00	0.00	588.15	493.29
02-02-01-7030	9.10	3.	4.	15.99	10.15	5.84	54.08	0.58	0.00	0.00	765.70	444.72
02-10-01-7030	5.60	3.	2.	18.15	13.95	4.20	54.96	0.68	0.00	0.00	367.41	278.26
99-01-01-9700	25.00	0.	0.	1.00	0.91	0.09	4.00	0.00	0.00	0.00	254.75	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF TISSUE SAMPLES JUNE 1978

CAPLINE ID	Dry Weight	Species Code	# Individuals	f <sub>1/2</sub> GC (µg/g)				CPI	INDIVIDUAL HYDROCARBONS (ng/g)				
				Total	Unresolved	Resolved	Total		1500	1708	2800	2900	
01-02-02-7010	16.70	1.	5.	11.54	10.54	1.00	9.60	0.00	11.80	9.70	0.00	196.60	
01-02-02-7060	4.00	6.	0.	74.84	70.05	4.79	32.80	0.00	0.00	0.00	263.20	0.00	
01-05-02-7060	91.50	6.	0.	118.42	109.42	9.00	91.50	0.00	132.10	541.60	585.00	0.00	
01-05-02-7061	1.40	6.	0.	11.18	9.73	1.45	146.00	0.00	0.00	0.00	0.00	0.00	
01-08-02-7010	35.00	1.	11.	9.59	8.99	0.60	7.10	0.00	15.70	2.90	65.50	41.70	
01-08-02-7011	24.60	1.	6.	13.12	12.42	0.70	225.20	0.00	0.00	27.90	45.70	26.10	
01-08-02-7012-1	13.30	1.	3.	9.16	8.19	0.97	148.30	0.00	16.20	27.90	81.50	45.70	
01-08-02-7012-2	12.60	1.	3.	22.42	2.07	20.35	46.00	0.00	0.00	36.20	42.30	38.10	
01-08-02-7012-3	12.30	1.	3.	9.84	9.20	0.64	11.40	0.00	26.30	9.80	30.70	18.50	
01-08-02-7060	0.50	6.	0.	84.73	83.76	0.97	184.00	0.00	0.00	0.00	974.00	0.00	
01-10-02-7010	20.60	1.	5.	39.69	35.80	3.89	50.00	0.00	9.20	19.70	352.50	344.20	
01-11-02-7060	1.30	6.	3.	244.40	242.28	2.12	365.00	0.00	0.00	0.00	0.00	0.00	
01-14-02-7010	19.20	1.	5.	18.13	16.55	1.58	12.50	0.00	18.50	33.10	162.50	202.60	
02-02-02-7030	9.10	3.	6.	16.70	15.69	1.01	17.70	0.00	11.60	12.30	111.20	106.60	
02-02-02-7070	16.90	7.	0.	129.97	68.41	61.56	893.00	0.00	0.00	668.10	0.00	0.00	
02-02-02-7080	1.10	7.	8.	171.91	163.17	8.74	124.00	0.00	0.00	589.60	1166.40	682.60	
02-05-02-7070	23.10	7.	0.	124.32	116.19	8.13	64.10	0.00	115.70	765.00	414.70	160.90	
02-05-02-7071	23.80	7.	5.	33.21	30.00	3.21	24.30	0.00	0.00	264.90	344.30	143.80	
02-05-02-7072	27.10	7.	0.	75.86	69.97	5.89	42.40	0.00	96.10	610.30	478.40	263.40	
02-08-02-7030	11.40	3.	6.	10.79	9.56	1.23	0.00	0.00	0.00	11.50	87.80	111.00	
02-08-02-7031	10.50	3.	6.	25.01	23.66	1.35	10.50	0.00	27.00	35.10	125.10	102.10	
02-08-02-7032	12.40	3.	8.	28.23	27.11	1.12	33.00	0.00	8.78	20.30	74.20	56.60	
02-08-02-7070	24.80	7.	0.	100.43	92.24	8.19	74.30	0.00	78.20	818.90	490.00	188.60	
02-10-02-7030	17.10	3.	13.	12.61	11.56	1.06	10.50	0.00	0.00	6.40	63.80	63.30	
02-11-02-7070	22.80	7.	0.	78.67	71.07	7.60	59.30	0.00	98.70	703.60	600.20	215.80	
02-14-02-7070	30.90	7.	0.	95.31	88.59	6.72	73.70	0.00	66.70	519.10	267.70	237.60	
99-01-02-6700	25.00	1.	0.	0.45	0.45	0.00	1.20	0.00	0.00	0.00	0.00	0.00	
99-02-02-9700	5.00	6.	0.	0.58	0.54	0.04	9.20	0.00	0.00	0.00	27.40	0.00	
99-03-02-9700	25.00	7.	0.	0.66	0.66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF TISSUE SAMPLES OCTOBER 1978

CAPLINE ID	Dry Weight	Species Code	# Individuals	INDIVIDUAL HYDROCARBONS (ng/g)				CPI	INDIVIDUAL HYDROCARBONS (ng/g)			
				f <sub>1/2</sub> GC (μg/g) Total	f <sub>1/2</sub> GC (μg/g) Unresolved	f <sub>1/2</sub> GC (μg/g) Resolved	f <sub>1/2</sub> GRAV (μg/g) Total		1500	1708	2800	2900
01-02-03-7010	15.90	1.	16.	20.59	19.18	0.53	12.93	0.43	8.88	11.25	3.91	1.78
01-02-03-7070	22.44	7.	5.	71.79	59.30	12.49	169.26	0.76	0.00	258.70	174.56	0.00
01-05-03-7080	9.46	8.	31.	57.90	55.47	2.43	53.69	0.18	17.03	127.87	191.96	30.61
01-08-03-7010	3.48	1.	2.	5.78	5.10	0.68	12.15	0.10	5.24	8.02	375.25	21.01
01-08-03-7070	22.37	7.	2.	33.40	28.14	5.25	58.92	0.28	41.28	282.85	218.20	0.00
01-10-03-7010	7.69	1.	5.	9.81	8.67	1.14	8.64	0.55	0.00	11.35	251.59	115.69
01-11-03-7080	4.88	8.	21.	317.06	309.79	7.27	218.06	0.32	21.76	111.01	978.56	133.03
02-02-03-7010	23.16	1.	10.	10.94	10.15	0.79	4.08	0.48	4.18	14.16	103.61	43.22
02-02-03-7080	2.07	8.	11.	52.03	50.38	1.65	51.39	0.31	0.00	44.90	333.83	67.51
02-05-03-7080	5.48	8.	30.	75.96	72.89	3.09	66.83	0.14	51.01	21.88	284.81	23.34
02-08-03-7010	19.85	1.	21.	8.67	7.91	0.77	9.68	0.55	1.24	9.29	68.41	31.83
02-08-03-7070	5.52	7.	1.	34.42	30.20	4.22	27.05	0.13	15.67	4.90	443.38	45.92
02-10-03-7010	17.60	1.	13.	12.06	11.12	0.94	4.50	0.78	1.42	31.01	51.37	44.49
02-11-03-7070	26.95	7.	2.	721.31	621.82	99.49	1295.27	0.00	3095.85	3324.08	0.00	0.00
02-14-03-7070	25.92	7.	3.	91.14	83.64	10.50	24.75	0.03	79.08	12.27	1312.68	26.67
99-01-03-9700	50.00	0.	0.	0.60	0.58	0.02	0.25	0.00	0.00	0.00	313.76	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF TISSUE SAMPLES, JANUARY 1979



CAPLINE ID	Dry Weight	Species Code	# Individuals	INDIVIDUAL HYDROCARBONS (ng/g)				CPI				
				f <sub>1/2</sub> GC (µg/g) Total	f <sub>1/2</sub> GC (µg/g) Unresolved	f <sub>1/2</sub> GC (µg/g) Resolved	f <sub>1/2</sub> GRAV (µg/g) Total		1500	1708	2800	2900
01-02-04-7010	13.30	1.	6.	25.80	17.55	8.25	47.07	0.00	0.00	46.50	50.50	148.87
01-02-04-7070	30.30	7.	5.	105.47	89.64	15.83	40.03	0.00	367.16	1588.88	489.00	145.09
01-05-04-7070	29.50	7.	7.	119.22	107.54	11.68	92.94	0.00	0.00	616.15	150.30	53.86
01-08-04-7010	11.60	1.	7.	111.19	105.58	5.61	50.65	0.00	0.00	0.00	384.60	1063.00
01-08-04-7070	27.60	7.	6.	118.49	101.29	17.20	69.51	0.00	154.92	933.04	345.80	106.00
01-10-04-7010	8.80	1.	6.	182.36	112.56	70.80	99.54	0.00	0.00	749.50	145.17	1308.33
01-11-04-7071	17.50	7.	12.	452.69	440.59	12.10	279.93	0.00	98.88	1054.84	33.80	119.28
01-11-04-7072	20.10	7.	12.	347.03	331.54	15.49	257.70	0.00	113.86	873.01	153.70	231.08
01-11-04-7073	24.30	7.	12.	347.00	336.00	109.00	84.26	0.00	9.90	474.70	152.30	100.50
01-14-04-7070	31.00	7.	7.	120.50	108.53	11.97	56.38	0.00	31.30	324.50	678.00	131.60
02-02-04-7010	8.40	1.	3.	141.42	76.94	64.48	146.84	0.00	0.00	1430.49	29.22	597.42
02-02-04-7080	14.40	8.	23.	124.06	123.09	0.97	79.78	0.00	1.20	16.60	40.30	43.10
02-05-04-7080	0.90	8.	5.	214.65	209.73	4.92	194.12	0.00	20.81	838.13	747.00	235.15
02-08-04-7070	16.40	7.	2.	83.84	76.29	7.55	67.24	0.00	33.43	889.30	265.00	281.29
02-08-04-7090	1.60	9.	13.	0.00	0.00	0.00	15.70	0.00	0.00	0.00	0.00	0.00
02-10-04-7090	10.20	9.	25.	12.81	11.76	1.05	6.44	0.00	0.00	11.99	7.40	10.95
02-11-04-7080	1.80	8.	7.	98.34	95.06	3.28	69.66	0.00	59.89	281.64	249.00	91.60
02-14-04-7080	4.20	8.	12.	86.33	82.91	3.42	83.02	0.00	8.79	271.33	30.84	99.43
99-03-04-9700	10.00	0.	0.	1.10	0.90	0.20	1.00	0.00	0.00	0.00	0.00	0.00
99-04-04-9700	16.00	0.	0.	0.59	0.55	0.04	2.94	0.00	0.00	0.00	0.00	0.00
99-05-04-9700	25.00	0.	0.	1.50	0.30	1.20	0.80	0.00	0.00	0.00	5.64	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF TISSUE SAMPLES, MAY 1979

CAPLINE ID	Dry Weight (g)	UV FLUORESCENCE PEAKS (µg/g Equivalents)				
		312 nm	327 nm	342 nm	405 nm	438 nm
01-02-01-6000	52.20	11.30	10.21	8.04	3.83	0.068
01-05-01-6000	50.30	13.10	10.97	8.60	3.72	0.078
01-08-01-6000	43.60	21.07	16.91	12.06	5.48	0.112
01-11-01-6000	42.40	15.68	13.77	10.69	4.52	0.116
01-14-01-6000	73.90	7.55	6.02	4.32	1.85	0.050
02-02-01-6000	77.70	2.96	2.38	1.57	0.42	0.011
02-05-01-6000	69.20	2.81	2.41	1.82	0.57	0.019
02-08-01-6000	73.30	3.21	2.82	2.22	0.80	0.017
02-11-01-6000	84.80	2.61	2.28	1.46	0.39	0.011
02-14-01-6000	72.70	2.02	1.74	0.97	0.18	0.004
99-01-01-9600	50.00	0.60	0.47	0.35	0.22	0.000
99-02-01-9600	100.00	0.02	0.00	0.00	0.00	0.000

CAPLINE ID	Dry Weight (g)	UV FLUORESCENCE PEAKS ( g/g Equivalents)				
		312 nm	327 nm	342 nm	405 nm	438 nm
01-02-02-6000	51.80	8.42	7.76	6.12	2.66	0.040
01-02-02-6001	63.60	8.02	7.00	4.54	1.06	0.029
01-02-02-6002	54.90	9.68	9.50	8.66	3.86	0.049
01-02-02-6003	62.40	7.24	7.48	6.78	3.12	0.029
01-02-02-6004	60.40	7.90	7.60	6.90	3.28	0.049
01-05-02-6000	36.70	11.24	10.64	8.94	3.72	0.070
01-08-02-6000	44.60	8.64	7.84	6.40	2.72	0.067
01-08-02-6000-2	39.30	14.80	13.96	11.18	4.30	0.078
01-08-02-6000-3	59.30	11.08	10.52	9.10	3.78	0.096
01-08-02-6001	37.20	14.24	13.10	10.52	4.08	0.084
01-08-02-6002	74.20	8.10	7.88	7.04	3.24	0.071
01-08-02-6003	61.00	9.84	9.74	8.42	3.86	0.051
01-08-02-6004	46.20	11.06	10.38	8.44	1.46	0.037
01-11-02-6000	59.40	10.72	10.16	8.64	3.66	0.063
01-14-02-6000	66.20	6.52	6.10	5.26	2.24	0.051
01-14-02-6001	62.70	11.20	9.40	6.24	2.32	0.060
01-14-02-6002	57.30	8.74	7.50	5.64	2.04	0.077
01-14-02-6003	50.60	10.26	9.88	8.50	3.68	0.060
01-14-02-6004	47.00	14.02	13.14	9.82	5.04	0.082
02-02-02-6000	111.50	2.98	2.48	1.68	0.48	0.012
02-02-02-6001	133.20	4.46	3.56	1.86	0.52	0.007
02-02-02-6002	90.50	2.70	2.22	1.32	0.44	0.007
02-02-02-6003	103.00	2.28	1.94	1.18	0.88	0.007
02-02-02-6004	90.80	4.48	4.02	2.54	0.82	0.017
02-05-02-6000	107.50	2.22	1.92	1.16	0.32	0.010
02-08-02-6000	112.60	1.74	1.60	1.20	0.36	0.009
02-08-02-6001	74.30	9.60	7.76	3.96	1.14	0.027
02-08-02-6002	86.90	2.24	1.98	1.24	0.34	0.007
02-08-02-6003	91.10	2.60	2.10	1.08	0.26	0.005
02-08-02-6004	87.80	2.64	2.34	1.66	0.66	0.011
02-11-02-6000	120.40	2.20	1.98	1.52	0.50	0.011
02-14-02-6000	101.70	1.82	1.58	1.08	0.34	0.008
02-14-02-6001	103.30	1.10	0.96	0.64	0.12	0.004
02-14-02-6002	97.10	2.66	1.46	0.58	0.06	0.003
02-14-02-6003	95.50	1.48	1.20	0.74	0.16	0.006
02-14-02-6004	96.10	2.12	1.80	1.24	0.32	0.010
99-01-02-9600	50.00	0.14	0.04	0.00	0.00	0.000
99-02-02-9600	50.00	0.00	0.00	0.00	0.00	0.000
99-03-02-9600	50.00	0.16	0.00	0.00	0.00	0.000

CAPLINE ID	Dry Weight (g)	UV FLUORESCENCE PEAKS ( $\mu\text{g/g}$ Equivalents)				
		312 nm	327 nm	342 nm	405 nm	438 nm
01-02-03-6000	88.00	2.52	2.78	2.35	1.14	0.014
01-05-03-6000	40.22	5.21	5.05	4.67	2.24	0.050
01-08-03-6000	38.43	5.56	7.61	8.50	3.65	0.060
01-11-03-6000	39.81	43.60	37.43	17.00	5.60	0.103
01-14-03-6000	48.92	4.48	4.74	4.78	1.95	0.022
02-02-03-6000	72.44	2.65	2.48	1.98	0.79	0.009
02-05-03-6000	80.44	0.96	0.88	0.70	0.25	0.003
02-08-03-6000	69.46	2.71	2.61	2.28	1.04	0.016
02-11-03-6000	76.57	0.58	0.53	0.39	0.12	0.002
02-14-03-6000	90.86	0.86	0.84	0.70	0.22	0.003
99-01-03-9600	100.00	0.14	0.09	0.06	0.02	0.000

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF BOTTOM SEDIMENTS JANUARY 1979

CAPLINE ID	Dry Weight (g)	UV FLUORESCENCE PEAKS (µg/g. Equivalents)				
		312 nm	327 nm	342 nm	405 nm	438 nm
01-02-04-6000	58.10	5.24	4.89	4.25	2.19	0.025
01-05-04-6000	56.80	14.01	11.66	8.62	3.69	0.066
01-08-04-6000	50.00	5.69	6.26	6.30	2.83	0.033
01-11-04-6000	52.00	53.59	38.76	17.87	4.39	0.509
01-14-04-6000	53.10	16.58	14.43	11.21	4.63	0.106
02-02-04-6000	89.00	3.27	2.78	1.82	0.65	0.021
02-05-04-6000	84.80	0.79	0.64	0.50	0.09	0.002
02-06-04-6000	84.00	1.23	0.99	0.75	0.31	0.031
02-11-04-6000	72.60	0.87	0.53	0.35	0.07	0.002
02-14-04-6000	74.40	1.08	0.78	0.55	0.19	0.002
99-01-04-9600	67.50	0.30	0.24	0.09	0.03	0.000

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF BOTTOM SEDIMENT SAMPLES, MAY 1979.

UV FLUORESCENCE PEAKS  
(µg/g Equivalents)

CAPLINE ID	Volume (l)	288 nm	312 nm	328 nm	348 nm
01-02-01-3001	10.00	1.34	1.51	2.95	0.00
01-05-01-3001	10.00	0.40	0.97	1.04	0.00
01-08-01-3001	10.00	154.40	4.93	4.93	0.00
01-11-01-3001	10.00	112.40	4.93	6.61	0.00
01-14-01-3001	10.00	0.32	1.76	1.73	0.00
02-02-01-3001	10.00	3.52	2.24	1.76	0.00
02-05-01-3001	10.00	161.10	3.70	3.70	0.00
02-08-01-3001	10.00	0.32	1.11	0.96	0.00
02-11-01-3001	10.00	0.33	1.29	1.12	0.00
02-14-01-3001	10.00	0.18	1.14	1.43	0.00
99-01-01-9300	10.00	0.35	0.59	0.81	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEAWATER SAMPLES JUNE 1978

CAPLINE ID	Volume (l)	UV FLUORESCENCE PEAKS (µg/g Equivalents)			
		288 nm	312 nm	328 nm	348 nm
01-02-02-3001	10.00	0.66	1.37	1.36	0.00
01-05-02-3001	10.00	0.60	2.19	2.31	0.00
01-05-02-3002	10.00	0.92	2.03	1.92	0.00
01-05-02-3003	10.00	1.27	3.40	3.56	0.00
01-08-02-3001	10.00	0.29	1.62	1.51	0.00
01-11-02-3001	10.00	3.97	26.26	22.39	0.00
01-14-02-3001	10.00	0.76	2.15	2.26	0.00
02-02-02-3001	10.00	0.05	0.64	0.52	0.00
02-05-02-3001	10.00	0.14	0.80	0.68	0.00
02-05-02-3002	10.00	0.05	0.87	0.76	0.00
02-05-02-3003	10.00	0.15	0.54	0.46	0.00
02-08-02-3001	10.00	0.09	1.47	1.21	0.00
02-11-02-3001	10.00	0.04	0.77	0.68	0.00
02-14-02-3001	10.00	0.04	0.51	0.44	0.00
99-01-02-9300	10.00	0.27	0.43	0.37	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEAWATER SAMPLES OCTOBER 1978

CAPLINE ID	Volume (l)	UV FLUORESCENCE PEAKS ( $\mu\text{g/g}$ Equivalents)			
		288 nm	312 nm	328 nm	348 nm
01-02-03-3001	10.00	0.00	4.34	2.80	0.59
01-05-03-3001	10.00	0.00	2.56	1.47	0.22
01-08-03-3001	10.00	0.00	3.79	2.61	1.20
01-11-03-3001	10.00	0.00	3.61	2.61	0.65
01-14-03-3001	10.00	0.00	5.89	5.24	1.09
02-02-03-3001	10.00	0.00	2.11	1.24	0.52
02-05-03-3001	10.00	0.00	1.56	0.87	0.15
02-08-03-3001	10.00	0.00	1.58	0.87	0.49
02-11-03-3001	10.00	0.00	0.84	0.52	0.31
02-14-03-3001	10.00	0.00	2.15	1.24	0.20
99-01-03-3001	10.00	0.00	0.01	0.00	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEAWATER SAMPLES JANUARY 1979



UV FLUORESCENCE PEAKS  
(µg/g Equivalents)

CAPLINE ID	Volume (l)	288 nm	312 nm	328 nm	348 nm	405 nm
01-02-04-3000	10.00	0.010	3.390	3.030	1.620	1.560
01-05-04-3000	10.00	0.010	2.520	2.110	0.950	0.940
01-08-04-3000	10.00	0.000	1.290	0.940	0.330	0.120
01-11-04-3000	10.00	0.000	1.970	1.580	0.490	0.250
01-14-04-3000	10.00	0.010	3.280	2.500	0.900	0.310
02-02-04-3000	10.00	0.000	2.410	2.220	1.240	1.780
02-05-04-3000	10.00	0.000	0.630	0.460	0.140	0.130
02-08-04-3000	10.00	0.020	0.540	0.450	0.300	0.350
02-11-04-3000	10.00	0.010	4.450	3.630	1.900	2.270
02-14-04-3000	10.00	0.010	4.670	3.550	0.840	0.510
99-02-04-9300	0.00	0.000	0.570	0.410	0.070	0.020

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CAPLINE PROJECT: HYDROCARBON ANALYSIS OF SEAWATER SAMPLES, May 1979

CAPLINE ID	Dry Weight	Species Code	# Individuals	UV FLUORESCENCE PEAKS (µg/g Equivalents)			
				302 nm	310 nm	325 nm	348 nm
01-02-01-7010	17.00	1.	3.	84.75	49.12	10.75	0.00
01-08-01-7010	24.40	1.	4.	26.03	11.57	0.77	0.00
01-10-01-7010	14.50	1.	2.	7.44	5.26	1.92	0.00
02-02-01-7030	9.10	3.	4.	2.36	3.19	1.94	0.00
02-10-01-7030	5.60	3.	2.	2.56	3.07	1.97	0.00
99-01-01-9700	25.00	0.	0.	4.58	2.18	0.34	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF TISSUE SAMPLES JUNE 1978

CAPLINE ID	Dry Weight	Species Code	# Individuals	UV FLUORESCENCE PEAKS (µg/g Equivalents)			
				302 nm	310 nm	325 nm	348 nm
01-02-02-7010	16.70	1.	5.	0.89	1.47	1.02	0.00
01-02-02-7060	4.00	6.	0.	2.11	2.43	1.78	0.00
01-05-02-7060	91.50	6.	0.	5.80	8.78	7.84	0.00
01-05-02-7061	1.40	6.	0.	1.77	3.14	2.58	0.00
01-08-02-7010	35.00	1.	11.	0.26	0.56	0.29	0.00
01-08-02-7011	24.60	1.	6.	1.08	1.56	0.50	0.00
01-08-02-7012-1	13.30	1.	3.	0.37	0.90	0.37	0.00
01-08-02-7012-2	12.60	1.	3.	0.10	0.35	0.00	0.00
01-08-02-7012-3	12.30	1.	3.	0.04	0.54	0.00	0.00
01-08-02-7060	0.50	6.	0.	4.02	4.97	3.78	0.00
01-10-02-7010	20.60	1.	5.	4.82	8.46	5.38	0.00
01-11-02-7060	1.30	6.	3.	0.24	0.31	0.24	0.00
01-14-02-7010	19.20	1.	5.	1.44	2.13	1.36	0.00
02-02-02-7030	9.10	3.	6.	1.99	2.83	1.82	0.00
02-02-02-7070	16.90	7.	0.	4.81	6.10	4.65	0.00
02-02-02-7080	1.10	7.	8.	6.70	8.41	6.48	0.00
02-05-02-7070	23.10	7.	0.	2.62	4.35	3.12	0.00
02-05-02-7071	23.80	7.	5.	0.21	0.27	0.20	0.00
02-05-02-7072	27.10	7.	0.	2.66	3.99	2.94	0.00
02-08-02-7030	11.40	3.	6.	1.29	1.85	1.19	0.00
02-08-02-7031	10.50	3.	6.	1.52	2.90	1.92	0.00
02-08-02-7032	12.40	3.	8.	1.63	2.79	2.17	0.00
02-08-02-7070	24.80	7.	0.	4.05	5.20	3.74	0.00
02-10-02-7030	17.10	3.	13.	0.93	1.29	0.92	0.00
02-11-02-7070	22.80	7.	0.	1.58	2.26	1.64	0.00
02-14-02-7070	30.90	7.	0.	5.80	9.69	7.05	0.00
99-01-02-6700	25.00	1.	0.	0.48	1.82	1.47	0.00
99-02-02-9700	5.00	6.	0.	0.06	0.08	0.06	0.00
99-03-02-9700	25.00	7.	0.	0.03	0.03	0.02	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF TISSUE SAMPLES OCTOBER 1978

UV FLUORESCENCE PEAKS  
(µg/g Equivalents)

CAPLINE ID	Dry Weight	Species Code	# Individuals	302 nm	310 nm	325 nm	348 nm
01-02-03-7010	15.90	1.	16.	0.00	1.76	1.22	0.32
01-02-03-7070	22.44	7.	5.	0.00	1.53	0.97	0.00
01-05-03-7080	9.46	8.	31.	0.00	4.41	3.11	0.17
01-08-03-7010	3.48	1.	2.	0.00	1.13	0.70	0.00
01-08-03-7070	22.37	7.	2.	0.00	3.14	2.20	0.39
01-10-03-7010	7.69	1.	5.	0.00	1.34	0.92	0.00
01-11-03-7080	4.88	8.	21.	0.00	33.08	24.95	4.21
02-02-03-7010	23.16	1.	10.	0.00	0.89	0.67	0.12
02-02-03-7080	2.07	8.	11.	0.00	3.56	2.62	0.53
02-05-03-7080	5.48	8.	30.	0.00	4.68	3.86	0.94
02-08-03-7010	19.85	1.	21.	0.00	0.97	0.77	0.15
02-08-03-7070	5.52	7.	1.	0.00	1.32	1.32	0.13
02-10-03-7010	17.60	1.	13.	0.00	1.15	0.91	0.16
02-11-03-7070	26.95	7.	2.	0.00	1.28	1.58	0.79
02-14-03-7070	25.92	7.	3.	0.00	3.69	2.85	0.54
99-01-03-9700	50.00	0.	0.	0.00	0.04	0.01	0.00

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF TISSUE SAMPLES, January 1979.

CAPLINE ID	Dry Weight	Species Code	# Individuals	UV FLUORESCENCE PEAKS (µg/g Equivalents)			
				302 nm	310 nm	325 nm	348 nm
01-02-04-7010	13.30	1.	6.	0.00	10.33	13.20	0.82
01-02-04-7070	30.30	7.	5.	0.00	1.92	1.49	0.37
01-05-04-7070	29.50	7.	7.	0.00	3.35	2.02	0.48
01-08-04-7010	11.60	1.	7.	0.00	8.13	8.13	0.04
01-08-04-7070	27.60	7.	6.	0.00	1.43	1.14	0.26
01-10-04-7010	8.80	1.	6.	0.00	7.65	9.62	1.61
01-11-04-7071	17.50	7.	12.	0.00	22.75	17.80	5.25
01-11-04-7072	20.10	7.	12.	0.00	26.20	20.61	5.53
01-11-04-7073	24.30	7.	12.	0.00	7.86	6.41	1.74
01-14-04-7070	31.00	7.	7.	0.00	2.09	1.66	0.39
02-02-04-7010	8.40	1.	3.	0.00	7.76	8.72	1.40
02-02-04-7080	14.40	8.	23.	0.00	6.24	4.89	1.28
02-05-04-7080	0.90	8.	5.	0.00	13.04	9.60	2.72
02-08-04-7070	16.40	7.	2.	0.00	2.54	1.80	0.55
02-08-04-7090	1.60	9.	13.	0.00	3.40	2.36	0.98
02-10-04-7090	10.20	9.	25.	0.00	0.74	0.57	0.18
02-11-04-7080	1.80	8.	7.	0.00	9.96	7.30	1.70
02-14-04-7080	4.20	8.	12.	0.00	5.89	4.61	1.32
99-03-04-9700	10.00	0.	0.	0.00	0.10	0.07	0.03
99-04-04-9700	16.00	0.	0.	0.00	0.06	0.04	0.02
99-05-04-9700	25.00	0.	0.	0.00	0.09	0.07	0.03

CAPLINE PROJECT: HYDROCARBON ANALYSIS OF TISSUE SAMPLES, MAY 1979.